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[LIST OF FILED DOCUMENT]

[DOCUMENT] Specification 1

[DOCUMENT] Abstract of the Disclosure 1

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[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION]

THERMAL RECORDING MATERIAL

[CLAIMS]

[Claim 1] A thermal recording material comprising, on a support, at least a thermal recording layer and a protective layer containing a water-soluble resin, wherein the thermal recording material comprises a water-soluble or oil-soluble compound of a transition element of the group IVb in the long-form periodic table.

[Claim 2] The thermal recording material of claim 1, wherein the protective layer contains ultrafine inorganic particles.

[Claim 3] The thermal recording material of claim 1, wherein the compound of a transition element is a water-soluble zirconium compound.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a thermal recording material for recording an image with a thermal head.

[0002]

[Prior Art]

The need for thermal recording systems is expanding in various fields such as facsimiles, printers, and labeling devices, and accompanying that need is a demand for thermal recording materials of higher performance.

In thermal recording materials for image recording by imagewise heating with a thermal head, it is important that the materials not only have properties matching the thermal head, the material and the shape of the protective film of the thermal head, but that they also stably produce high-quality images without generating dirt or abrasions in the thermal head.

[0003]

A protective layer is often provided on an outermost print surface of a thermal recording material, therefore, the suitability of a thermal recording material is often determined by its performance in relations to the protective layer of the thermal head. The glossiness of the thermal recording material can be improved to a certain extent by increasing the content of the hardening agent in the protective layer. However, if the amount of hardening agent exceeds a certain level, this results in

the drawback of deteriorating the surface condition of the image recording surface (causing surface coarseness), thereby deteriorating surface gloss.

Moreover, when high-speed printing is executed while the interior of the printing apparatus is cold, for example, at the start of a printing operation, water drops condensed on the surface of the thermal head may stick to the outermost print surface. Such water drops sticking to the outermost print surface cause gloss unevenness, thus constituting a factor in image quality deterioration.

It has therefore been a major issue to provide a thermal recording material capable of realizing high surface gloss and improved color forming sensitivity, and able to stably provide high-quality images.

[0004]

[Problems to be Solved by the Invention]

The invention was made in view of the above problems and is to provide a thermal recording material having high glossiness and the capability to prevent deterioration in the printing sheet, thereby providing high-quality images.

[0005]

[Means for Solving The Problems]

The aforementioned objects was solved by the

following invention. The present invention provides:

<1> A thermal recording material comprising, on a support, at least a thermal recording layer and a protective layer containing a water-soluble resin, wherein the thermal recording material comprises a water-soluble or oil-soluble compound of a transition element of the group IVb in the long-form periodic table.

[0006]

<2> The thermal recording material of <1>, wherein the protective layer contains ultrafine inorganic particles.

[0007]

<3> The thermal recording material of <1> or <2>, wherein the compound of a transition element is a water-soluble zirconium compound.

[0008]

[Embodiment]

The thermal recording material of the present invention is characterized in that it includes, on a support, a thermal recording layer and a protective layer containing a water-soluble resin, and includes a water-soluble or oil-soluble compound of transition element of a group IVb. It is preferred that the protective layer

includes ultrafine inorganic particles and that the transition element compound is a water-soluble zirconium compound.

[0009]

In the thermal recording material of the invention, the presence of the water-soluble or oil-soluble compound of transition element of a group IVb can improve water-resistance of images and image quality. As a result, the thermal recording material of the present invention can maintain surface smoothness, thereby providing high gloss. Further, even with high-speed printing when the interior of the printing apparatus is cold, for example, at the start of a printing operation, it is possible to reduce image quality deterioration resulting from water drops condensed on the surface of the thermal head, thereby stably providing a high-quality image.

[0010]

Another layer suitably selected according to purpose may be provided between the aforementioned support and protective layer. Examples of such other layers include an undercoat layer provided between the support and the thermal recording layer, an intermediate layer provided between the thermal recording layers, and a light

transmittance control layer provided between the thermal recording layer and the protective layer.

Hereafter, the thermal recording material of the invention will be explained in detail.

[0011]

(A compound of transition element of a group IVb)

The invention is characterized by the fact that the aforementioned compound of transition element of a group IVb is contained in a water-soluble state or an oil-soluble state in the thermal recording material. As the compound of transition element of a group IVb in the invention, it is preferable to use a zirconium compound or a titanium compound, more preferable to use a zirconium compound.

[0012]

Preferred examples of the water-soluble zirconium compound include ZrOCO_3 , $\text{ZrO}(\text{NO}_3)_2$, ZrOSO_4 , $\text{ZrO}(\text{CH}_3\text{COO})_2$, $(\text{NH}_4)_2\text{ZrO}(\text{CO}_3)_2$, $\text{Zr}(\text{OC}_4\text{H}_9)_3(\text{C}_5\text{H}_7\text{O}_2)$, $\text{Zr}(\text{OC}_4\text{H}_9)_2(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Zr}(\text{OC}_4\text{H}_9)_3(\text{C}_6\text{H}_9\text{O}_3)$, $\text{Zr}(\text{OC}_4\text{H}_9)(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_6\text{H}_9\text{O}_3)_2$, and $\text{Zr}(\text{OC}_4\text{H}_9)_3(\text{OCOC}_{17}\text{H}_{35})$. Among these, as the water-soluble zirconium compound, $\text{ZrO}(\text{NO}_3)_3$, ZrOSO_4 , and $(\text{NH}_4)_2\text{ZrO}(\text{CO}_3)_2$ are more preferred.

[0013]

Preferred examples of the oil-soluble zirconium compound include $\text{ZrO}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$, $\text{ZrO}(\text{C}_{14}\text{H}_{27}\text{O}_2)_2$, $\text{ZrO}(\text{C}_{12}\text{H}_{23}\text{O}_2)_2$, and $\text{ZrO}(\text{C}_8\text{H}_{15}\text{O}_2)_2$, and $\text{ZrO}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ is more preferred as the oil-soluble zirconium compound.

[0014]

Preferred examples of the water-soluble titanium compound include $(\text{OH})_2\text{Ti}(\text{C}_3\text{H}_5\text{O}_3)_2$, $(\text{C}_6\text{H}_{14}\text{O}_3\text{N})_2\text{Ti}(\text{C}_3\text{H}_7\text{O})_2$, $(\text{C}_8\text{H}_{17}\text{O})_2\text{Ti}(\text{C}_8\text{H}_{17}\text{O}_2)_2$, $(\text{C}_3\text{H}_7\text{O})_2\text{Ti}(\text{C}_6\text{H}_9\text{O}_3)_2$, $\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_4$, and $(\text{C}_3\text{H}_7\text{O}_2)\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$. Also, preferred examples of the oil-soluble titanium compound include $\text{Ti}(\text{OH})_2(\text{OCOC}_{17}\text{H}_{35})_2$ and $\text{Ti}(\text{OH})_2(\text{OCOC}_{19}\text{H}_{39})_2$.

[0015]

In the thermal recording material of the invention, a layer which includes the aforementioned water-soluble or oil-soluble compound of transition element of a group IVb is not particularly limited. However, the compound of transition element of a group IVb is preferably included in the protective layer or the intermediate layer, more preferably in the protective layer. When adding the compound of the aforementioned compound of transition element in the protective layer, in case of the water-soluble compound of transition element of a group IVb, it

is necessary to pay attention to liquid stability, including reactivity thereof. Also in case of adding the oil-soluble compound of transition element of a group IVb in the protective layer, it is necessary to pay attention to dispersion stability since the oil-soluble compound of transition element of a group IVb is added in an emulsion.

[0016]

In case of adding the compound of transition element of a group IVb in the protective layer, the content is preferably 0.1 to 25 %, more preferably 0.5 to 20 % by mass and further preferably 1 to 15 % by mass. If the content of the compound of transition element of a group IVb is within a range of 0.1 to 25 % by mass, adequate water-resistance can be obtained and deterioration of the gloss, resulting from inferior surface smoothness when coating and drying, does not occur.

[0017]

<Protective layer>

The protective layer in the thermal recording material of the invention is provided for preventing sticking of the thermal recording layer and for protecting the thermal recording layer from solvent or or the like. The protective layer includes a water-soluble resin,

preferably includes ultrafine inorganic particles and a heat melting lubricant, and silicon modulated acryl emulsion, in addition to the water-soluble resin. The protective layer may contain other various additives if necessary.

[0018]

(Water-soluble resin)

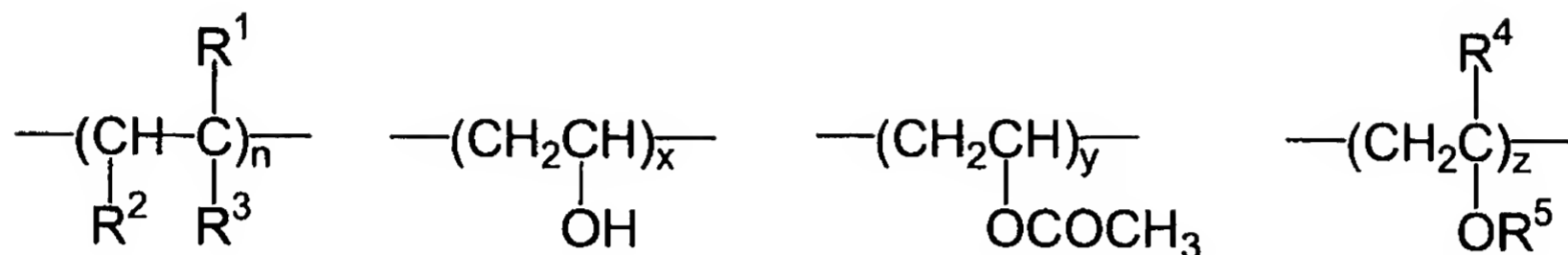
The aforementioned water-soluble resin is preferably modified polyvinyl alcohol, and particularly preferably a long-chain alkyl ether-modified polyvinyl alcohol. The use of long-chain alkyl ether-modified polyvinyl alcohol improves dispersibility of the ultrafine inorganic particles, thereby maintaining the smoothness of the surface of the thermal recording material and suppressing decreases in glossiness resulting from the addition of the ultrafine inorganic particles.

[0019]

The long-chain alkyl ether-modified polyvinyl alcohol preferably includes an alkyl group with 8 to 20 carbon atoms. The long-chain alkyl ether-modified polyvinyl alcohol is more preferably a polymer represented by the following general formula (A):

[0020]

General formula (A)



[0021]

In general formula (A), R^1 represents a hydrogen atom, a methyl group or $-\text{CH}_2\text{CO}_2\text{M}$; R^2 represents a hydrogen atom, or $-\text{CO}_2\text{M}$; R^3 represents a hydrogen atom, $-\text{CO}_2\text{M}$, an amino group, an amido group, a substituted amido group, a hydroxyl group, a glycidyl group, a sulfonic acid group, a polyethylene oxide group, a polypropylene oxide group or a group having these functional groups; and R^4 represents a hydrogen atom or a methyl group.

The combination is preferred in which R^1 , R^2 and R^4 are hydrogen atoms and R^3 is $-\text{CO}_2\text{M}$, or a combination in which R^2 and R^4 are hydrogen atoms, R^1 is $-\text{CH}_2\text{CO}_2\text{M}$ and R^3 is $-\text{CO}_2\text{M}$.

[0022]

In the foregoing general formula (A), M represents a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, Na, K or Li.

[0023]

In the foregoing general formula (A), R^5 represents a long-chain alkyl group i.e., an alkyl group (with 8 or more carbon atoms, preferably 8 to 20 carbon atoms). The alkyl group may be a normal chain or a branched chain. Also, the alkyl group may have a substituent such as an aryl group. The alkyl group is more preferably with 8 to 16 carbon atoms for improving a lubricating property, and particularly preferably, a dodecyl group with 12 carbon atoms.

[0024]

In the foregoing general formula (A), n , x , y and z each represent a degree of polymerization. n is preferably 0 to 20, more preferably 0 to 10. A large value of n increases acidic groups, thereby improving mutual solubility with gelatin. In order to exploit the characteristics of polyvinyl alcohol, such as a gas barrier property at or under T_g (glass transition point), x is preferably 60 to 99, more preferably 75 to 95. Also, y is preferably 0 to 20. A value of z is preferably larger in consideration of friction resistance with the thermal recording head and lubricating property. However, since z is limited by the solubility and viscosity of an

aqueous solution, it is preferably within a range of 0.5 to 10 % based on the total sum of n, x, y and z, more preferably 1 to 5 %.

[0025]

The aforementioned long-chain alkyl ether-modified polyvinyl alcohol preferably has a Tg of 50°C or higher, more preferably 60°C or higher. Scratch resistance is also not deteriorated when the glass transition point (Tg) is equal to or higher than 50°C.

[0026]

The long-chain alkyl ether-modified polyvinyl alcohol is preferably contained in an amount of 50 % by mass or higher in the total binder of the protective layer, and more preferably at 80 % by mass or higher. Adjusting the content of the long-chain alkyl ether-modified polyvinyl alcohol so as to be equal to or higher than 50 % by mass allows the long-chain alkyl ether-modified polyvinyl alcohol to fully exhibit the aforementioned characteristics.

[0027]

Long-chain alkyl groups tend to orient easily on the surface of a protective layer employing the long-chain

alkyl ether-modified polyvinyl alcohol. Such a surface reduces printing torque, thereby avoiding printing failure, and it is therefore possible to improve smoothness (glossiness) of the print surface and color developing density. Also, decreased static friction and dynamic friction on the surface of the protective layer provide good running ability of a medium on a printer. Furthermore, the long-chain alkyl ether-modified polyvinyl alcohol not only exhibits characteristics of excellent light fastness and film strength, which characterize the polyvinyl alcohol system, but also has hydrophobic groups oriented on the surface, which improves the water-resistance of the protective layer.

[0028]

In the protective layer of the invention, in addition to the long-chain alkyl ether-modified polyvinyl alcohol, another binder may also be employed if necessary. Examples of such binders include a water-soluble polymer such as vinyl acetate-acrylamide copolymer, silicon-modified polyvinyl alcohol, starch, denatured starch, methyl cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, gelatin, gum Arabic, casein, a hydrolysate of a styrene-maleic acid copolymer, a hydrolysate of a styrene-maleic acid copolymer half ester, a hydrolysate of an

isobutylene-maleic anhydride copolymer, a polyacrylamide derivative, polyvinylpyrrolidone, sodium polystyrenesulfonate, and sodium alginate, and a synthetic rubber latex or a synthetic resin emulsion such as a styrene-butadiene rubber latex, an acrylonitrile-butadiene rubber latex, a methyl acrylate-butadiene rubber latex or a vinyl acetate emulsion.

[0029]

Among these binders, polyvinyl alcohol or a derivative thereof are preferred (hereinafter, collectively referred to as "polyvinyl alcohol"), and specific examples include those described in JP-A No. 2000-118133.

[0030]

A polymer constituting the aforementioned binder has a Tg of 150°C or lower, preferably of 0°C to 130°C and particularly preferably of 40°C to 100°C.

[0031]

The content amount of the binder in the protective layer is preferably 25 to 80 % by mass based on the entire protective layer, and more preferably 40 to 70 % by mass.

[0032]

(Ultrafine inorganic particles)

The protective layer of the invention preferably includes ultrafine inorganic particles. The inclusion of ultrafine inorganic particles having small particle sizes make it possible to maintain high hardness without varying the smoothness of the surface.

[0033]

The term "ultrafine inorganic particles" refers to fine inorganic particles with an average primary particle size of 0.5 μm or less, preferably 0.2 μm or less and more preferably, of 0.15 μm or less. Any fine inorganic particles fulfilling these conditions may be employed without any particular restriction, however, they preferably have a maximum particle size in a dispersion (i.e., a threshold level at a larger side in the particle size distribution in a dispersion) of 0.5 μm or less, more preferably 0.4 μm or less, and particularly preferably of 0.35 μm or less. In the ultrafine inorganic particles, it is preferred that the frequency of (coagulated) particles having an average particle size of 0.35 μm or larger in a dispersion is 5% or less, preferably 1% or less. It is particularly preferred that the frequency of (coagulated) particles having an average particle size of 0.25 μm or

larger in a dispersion is 5% or less. Such particle size can be measured by known methods, for example, by using a submicron particle size analyzer Coulter N4 manufactured by Nikkaki Co.

[0034]

The ultrafine inorganic particles can be, for example, colloidal silica, barium sulfate, zinc oxide, magnesium oxide, lead oxide, zirconium oxide, or alumina, among which preferred are colloidal silica, barium sulfate or alumina, and particularly preferred are colloidal silica or barium sulfate.

[0035]

Specific examples of ultrafine inorganic particles advantageously employable in the invention include barium sulfate (trade name: BARIFINE BF-21, BF-20, manufactured by Sakai Chemical Industries, Co.), colloidal silica (trade name: Snotex O, manufactured by Nissan Chemical Ltd.), zirconium oxide (trade name: NZR-A, manufactured by Nissan Chemical Ltd.), zinc oxide (trade name: FINEX-75, Sakai Chemical Industries, Co.), titanium oxide (trade name: TTO-55, manufactured by Ishihara Sangyō Co.), and silica manufactured by Nippon Aerosil Co.

[0036]

The protective layer of the invention preferably includes two or more types of ultrafine inorganic particles of different particle sizes, such as the preferable combination of barium sulfate and colloidal silica. Use of colloidal silica of small particle size maintains high hardness without varying the smoothness of the surface, however, if colloidal silica alone are used, the lubricant may diffuse and may not be retained on the surface of the thermal recording material due to colloidal silica's high hydrophilicity. However, a combined use of barium sulfate retains the necessary amount of lubricant stably on the surface of the thermal recording material. Thus, the thermal recording material of the invention maintains surface smoothness, thereby achieving high gloss while maintaining high hardness on the surface. Further, the thermal recording material of the invention, which stably retains the lubricant on the surface, is capable of preventing dirtying of the thermal head, thereby being capable of stably providing a high-quality image.

[0037]

The average particle size of barium sulfate is preferably 0.05 to 0.20 μm , and more preferably 0.10 to 0.15 μm . The average particle size of colloidal silica is

preferably 10 to 50 nm, more preferably 10 to 30 nm, and particularly preferably 15 to 25 nm. The content of the colloidal silica in the protective layer is preferably 8 to 24 % by mass based on barium sulfate, more preferably 8 to 16 % by mass, and particularly preferably 8 to 10 % by mass. If the particle sizes of barium sulfate and colloidal silica are not within the above-mentioned ranges, and the proportion of contents of barium sulfate and colloidal silica is not within the above-mentioned range, it may become impossible to maintain high glossiness, or the recording head may exhibit enhanced dirt, thereby making the formation of a plurality of good images difficult.

[0038]

The barium sulfate and colloidal silica are preferably contained in an amount of 60 % by mass or higher in the total ultrafine inorganic particles, more preferably 75 % by mass or higher and particularly preferably 85 % by mass or higher. Presence of barium sulfate and colloidal silica in an amount of 60 % by mass or higher ensures that the aforementioned effects can be fully exhibited.

[0039]

Upon considering the obtained effects and practical manufacturing, it is preferable to add the ultrafine inorganic particles by employing a method of addition utilizing a resin solution containing an aqueous dispersible resin such as carboxymethyl cellulose, gelatin or polyvinyl alcohol; or a method of addition utilizing colloidal dispersion prepared in various mills. These methods are preferably employed in order to avoid mutual coagulation of the fine particles and to achieve a uniform adsorption on the surface of the resin particles.

Also a proportion of the binder and the ultrafine inorganic particles (binder/ultrafine inorganic particles) in a mass ratio is preferably 0.8/0.5 to 0.8/0.15, and more preferably 0.8/0.45 to 0.8/0.3.

[0040]

An inorganic layered compound such as mica, or a pigment such as calcium oxide, zinc oxide, titanium oxide, aluminum hydroxide, caolin, a synthetic silicate salt, amorphous silica or an urea-formalin resin powder may be added to the protective layer.

[0041]

(Hardening agent)

In the protective layer of the invention, a

hardening agent is preferably employed in combination with the binder in order to elevate the degree of hardening of the protective layer. Examples of such hardening agents include a vinylsulfone compound, an aldehyde compound (such as formaldehyde or glutaraldehyde), an epoxy compound, an oxazine compound, a triazine compound, a methylated melamine, a blocked isocyanate, a methylool compound, a carbodimide resin or a boron compound.

Among these hardening agents, a boron compound is preferred as it causes a prompt crosslinking reaction with polyvinyl alcohol without requiring the addition of a reaction accelerator or a high-temperature process. Particularly preferred boron compounds include boric acid or borax.

[0042]

When coating the protective layer and the thermal recording layer in a multilayer coating (simultaneous coating), the hardening agent need not necessarily be added in a coating solution for the protective layer. The hardening agent may be contained, for example, in a coating solution for an intermediate layer. Also, when employing boric acid as the hardening agent, the amount is preferably 18 to 30 % by mass, and more preferably 20 to 27 % by mass, based on the total amount of the long-chain

alkyl ether-modified polyvinyl alcohol, polyvinyl alcohol employed as the binder of the protective layer, and polyvinyl alcohol contained in the thermal recording layer, intermediate layer, etc., which will be further explained later (i.e., the total amount of polyvinyl alcohol contained in layers on the recording surface side of the thermal recording material).

If the boric acid contained is less than 18 % by mass based on the total amount of polyvinyl alcohol employed in the thermal recording material, the protective layer may not be sufficiently hardened or strengthened, and if the boric acid contained exceeds 30 % by mass, diffusion of the lubricant when printing is facilitated, thereby preventing a decrease in the hydrophobicity of the surface of the protective layer, which leads to deterioration in image quality or glossiness.

[0043]

(Heat melting lubricant)

In order to achieve smooth printing without printing failures such as sticking, the protective layer of the invention preferably includes a heat melting lubricant, so as to reduce friction between the surface of the thermal recording material and the thermal head when printing.

The term "heat melting lubricant" refers to a fatty acid derivative having a melting point of 30°C or higher.

Well-known heat melting lubricants suitably selected for their heat melting properties may be used. Specific examples include a higher alcohol, a higher fatty acid, a higher fatty acid metal salt, a higher fatty acid ester, and a higher fatty acid glyceride, the preferred being the higher fatty acid metal salt.

[0044]

The content of the heat melting lubricant in the protective layer of the invention is preferably within a range of 10 to 40 % by mass based on the binder of the protective layer, and more preferably 15 to 25 % by mass. When the content of the heat melting lubricant in the protective layer is 10% by mass or less, the heat melting lubricant can sufficiently reduce printing torque, and can sufficiently facilitate deteriorations of various characteristics such as decreased glossiness resulting from excessive print surface deformation, or increased background coloration when irradiated by light.

[0045]

(Silicon modified acryl emulsion)

It is preferable to include silicon modified acryl

emulsion in the protective layer of the invention for maintaining hydrophilicity on the surface of the protective layer.

The abovementioned silicon modified acryl emulsion can be obtained by various methods and preferably obtained with an organic silicon monomer having a polymeric unsaturated group and a hydrolysis group in a molecule and a mixture of a monomer comprising acrylic acid ester or meta acrylic acid ester are emulsified in an aqueous vehicle.

[0046]

The abovementioned acrylic acid ester or the meta acrylic acid ester is preferably alkyl ester and is particularly preferably alkyl ester having an alkyl group with 1 to 10 carbon atoms.

The abovementioned silicon monomer includes, for example, vinyl trimethoxy silane, vinyl triethoxy silane, vinyl tributoxy silane, aryl triethoxy silane, trimethoxy silyl propyl aryl amine, γ -(meta) acryloxy propyl trimethoxy silane, 2 styryl ethyl trimethoxy silane, vinyl triacetoxysilane, and the like.

[0047]

The content amount of the silicon modified acryl

emulsion in the protective layer of this invention is preferably 10 to 40% by mass based on the heat melting lubricant and more preferably 15 to 25% by mass. When the content amount of the silicon modified acryl emulsion in the protective layer is less than 10% by mass based on the heat melting lubricant, the hydrophobicity of the printing surface of the protective layer cannot be sufficiently maintained, and if it exceeds 40% by mass, sufficient lubricating property at the time of printing may not be given.

[0048]

(Method for forming protective layer)

The protective layer of the invention can be formed on a thermal recording layer (described below) by coating a protective layer coating solution, which includes a binder and ultrafine inorganic particles, etc., with a coating apparatus such as a bar coater, an air knife coater, a blade coater or a curtain coater, and then drying the layer. However, the protective layer may also be simultaneously coated with the other layers such as the thermal recording layer via a superposition method, or by coating after the other layers have been coated and dried. The amount of dry coating of the protective layer is preferably within a range of 0.1 to 3 g/m², and more

preferably 0.3 to 2.0 g/m². An excessive amount of coating may result in significant loss of thermal sensitivity, while an excessively low amount may be unable to exhibit the desired functions (e.g., friction resistance, lubricating property, scratch resistance, etc.) of the protective layer. After the coating, the protective layer may be subjected to a calendaring process if necessary.

[0049]

In the protective layer, in addition to the ultrafine inorganic particles (pigment), it is also preferable to add components such as another pigment, a wax, a catalyst, a releasing agent, a surfactant, or a water-repellent agent if necessary.

[0050]

<Thermal recording layer>

The thermal recording layer may have a single-layer structure or a multi-layer structure. The thermal recording layer may have a layer structure suitably selected according to the purpose.

The thermal recording layer includes a color forming component and is designed so as to form an image of a desired color by a color forming reaction of the color forming component. The color forming component is not

particularly limited, and known component may be advantageously employed. The color forming reaction is also not particularly restricted, for example, the color forming reaction of a diazonium salt compound and a coupler, or the color forming reaction of an electron donating colorless dye and an electron accepting compound can be advantageously employed.

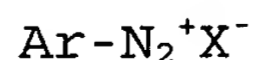
[0051]

When the thermal recording layer includes a diazonium salt compound and a coupler capable of color formation by reacting therewith when heated, a basic substance capable of accelerating the color forming reaction of the diazonium compound and the coupler is advantageously added to the thermal recording layer.

[0052]

The aforementioned diazonium salt compound is a compound represented by the following general formula (B). In the compound represented by general formula (B), the maximum absorption wavelength thereof can be controlled by adjusting the position and type of substituent in the Ar portion.

General formula (B):



In general formula (B), Ar represents an aryl group, and X⁻ represents an acid anion.

[0053]

Specific examples of the diazonium salt compound include acid anion salts such as:

4-(N-(2-(2,4-di-tert-amylphenoxy)butyryl)piperadino)benzene diazonium;

4-dioctylaminobenzene diazonium;

4-(N-(2-ethylhexanoyl)piperadino)benzene diazonium;

4-dihexylamino-2-hexyloxybenzene diazonium;

4-N-ethyl-N-hexadecylamino-2-ethoxybenzo diazonium;

3-chloro-4-dioctylamino-2-octyloxybenzene diazonium;

2,5-dibutoxy-4-morpholinobenzene diazonium;

2,5-octoxy-4-morpholinobenzene diazonium;

2,5-dibutoxy-4-(N-(2-ethylhexanoyl)piperadino)benzene diazonium;

2,5-diethoxy-4-(N-(2-(2,4-di-tert-amylphenoxy)butyryl)-piperadino)benzene diazonium;

2,5-dibutoxy-4-tolylthiobenzene diazonium; or

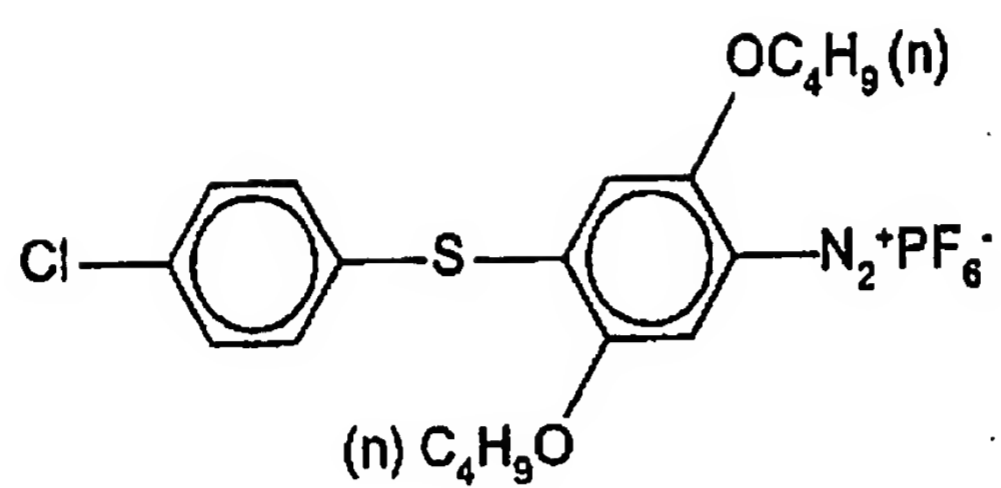
3-(2-octyloxyethoxy)-4-morpholinobenzene diazonium, and the following diazonium salt compounds (D-1 to D-5). These compounds may be used singly or in combination of two or more types.

Among these, particularly preferred are a

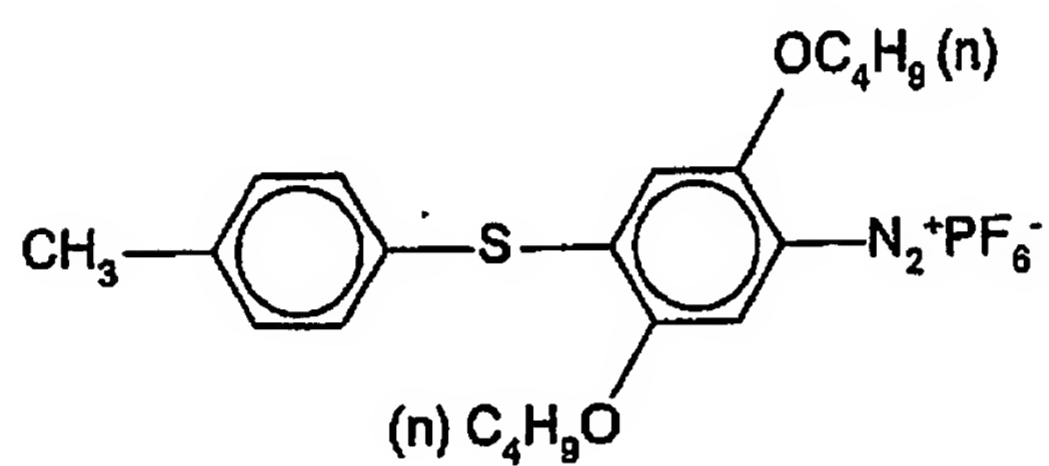
hexafluorophosphate salt, a tetrafluoroborate salt and a 1,5-naphthalenesulfonate salt.

[0054]

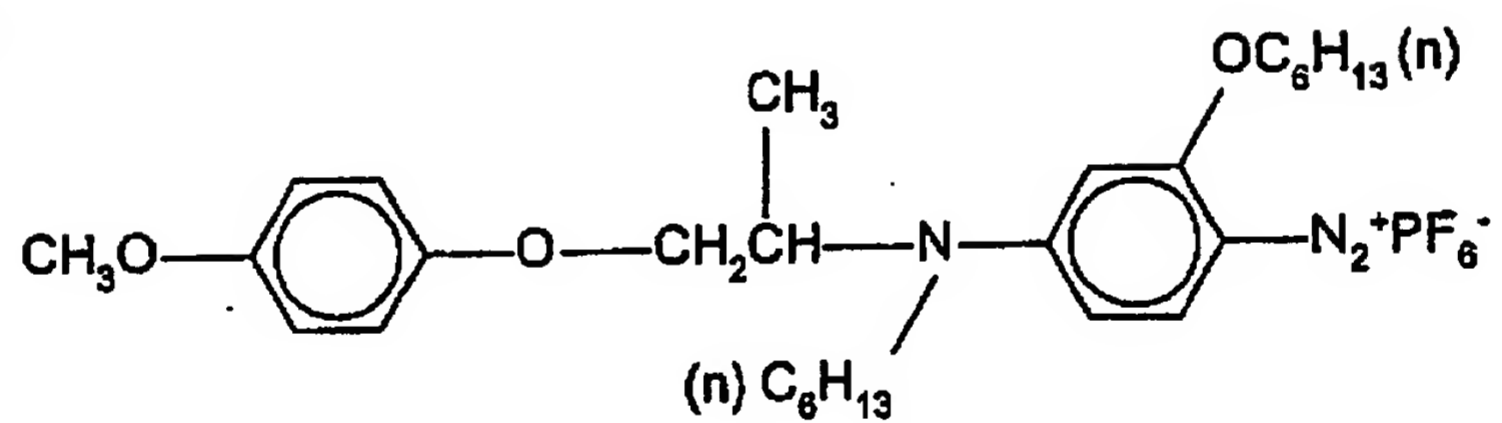
D-1



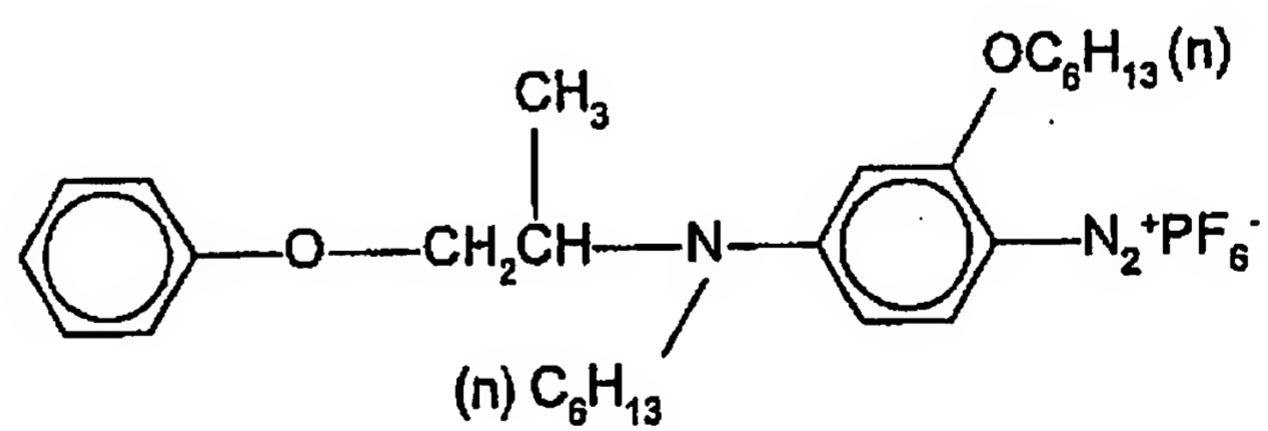
D-2



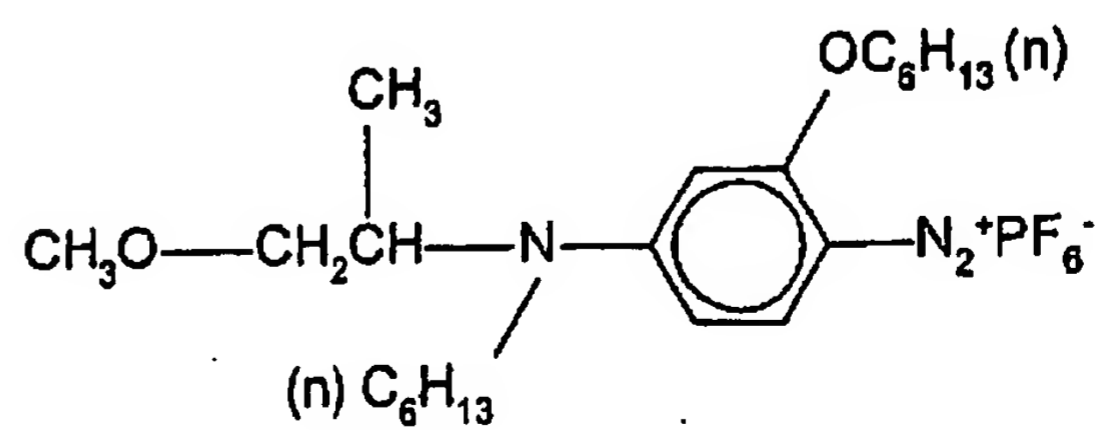
D-3



D-4



D-5



[0055]

Among these diazonium salt compounds, particularly preferred are those decomposable by light of a wavelength of 300 to 400 nm, which are 4-(N-(2-(2,4-di-tert-amylphenoxy)butyryl)piperadino) benzene diazonium; 4-dioctylaminobenzene diazonium; 4-(N-(2-ethylhexanoyl)piperadino)benzene diazonium; 4-dihexylamino-2-hexyloxybenzene diazonium; 4-N-ethyl-N-hexadecylamino-2-ethoxybenzo diazonium; 2,5-dibutoxy-4-(N-(2-ethylhexanoyl)piperadino)benzene diazonium; 2,5-diethoxy-4-(N-(2-(2,4-di-tert-amylphenoxy)butyryl)-piperadino)benzene diazonium, and the diazonium salt compounds represented in examples D-3 to D-5.

The maximum absorption wavelength of the diazonium compound is obtained by measurement of each diazonium salt compound in a coated film of a coating amount of 0.1 to 1.0 g/m², with a spectrophotometer (trade name MPS-2000, manufactured by Shimadzu Mfg. Co.).

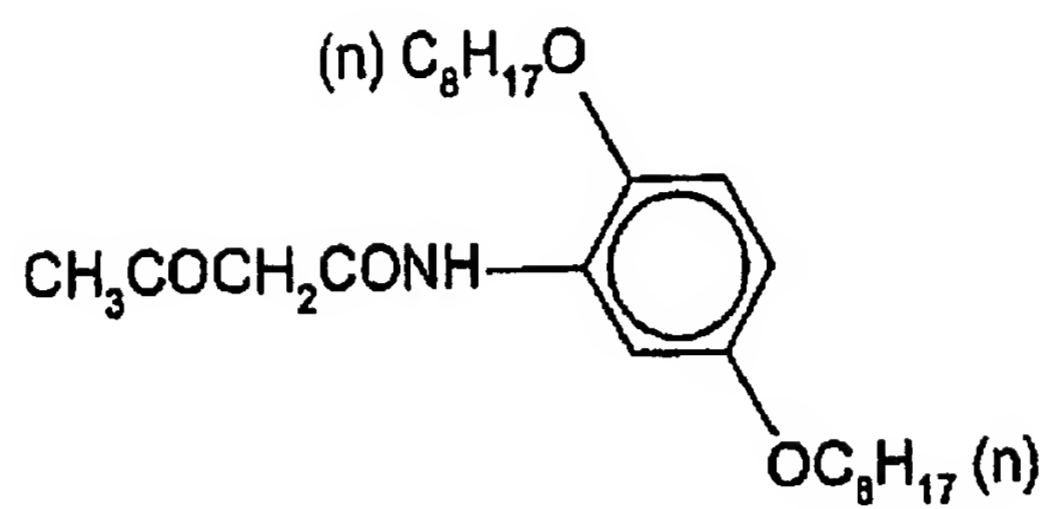
[0056]

Examples of couplers capable of color formation by reaction with the diazonium compound in a heated state include resorcin; phloroglucin; sodium 2,3-dihydroxynaphthalene-6-sulfonate; 1-hydroxy-2-naphthoic

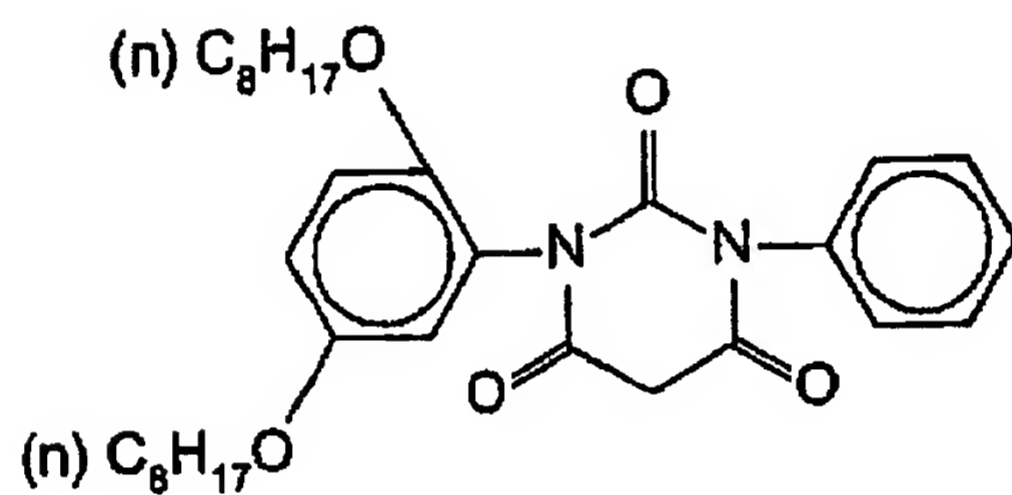
acid morpholinopropylamide; 1,5-dihydroxynaphthalene; 2,3-dihydroxynaphthalene; 2,3-dihydroxy-6-sulfanylnaphthalene; 2-hydroxy-3-naphthoic acid anilide; 2-hydroxy-3-naphthoic acid ethanolamide; 2-hydroxy-3-naphthoic acid octylamide; 2-hydroxy-3-naphthoic acid N-dodecyloxypropylamide; 2-hydroxy-3-naphthoic acid tetradecylamide; acetanilide; acetoacetanilide; benzoylacetanilide; 2-chloro-5-octylacetoacetanilide; 1-phenyl-3-methyl-5-pyrazolone; 1-(2'-octylphenyl)-3-methyl-5-pyrazolone; 1-(2',4',6'-trichlorophenyl)-3-benzamide-5-pyrazolone; 1-(2',4',6'-trichlorophenyl)-3-anilino-5-pyrazolone; 1-phenyl-3-phenylacetamide-5-pyrazolone; and the following compounds (C-1 to C-6). These couplers may be used singly or in combination of two or more types.

[0057]

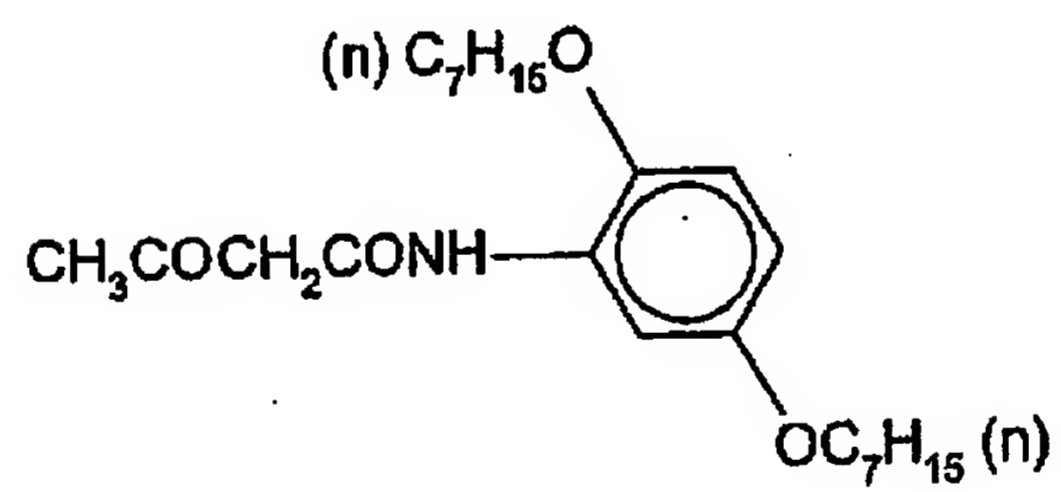
C-1



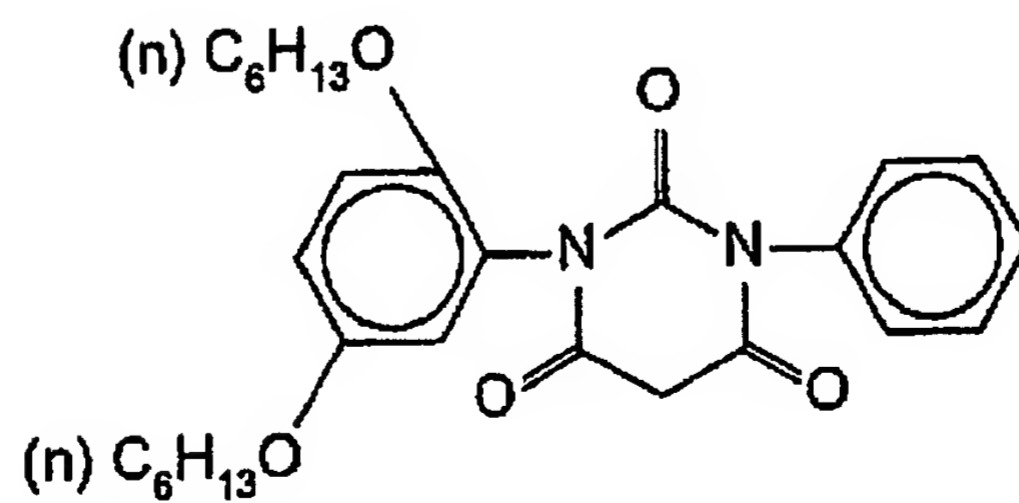
C-2



C-3

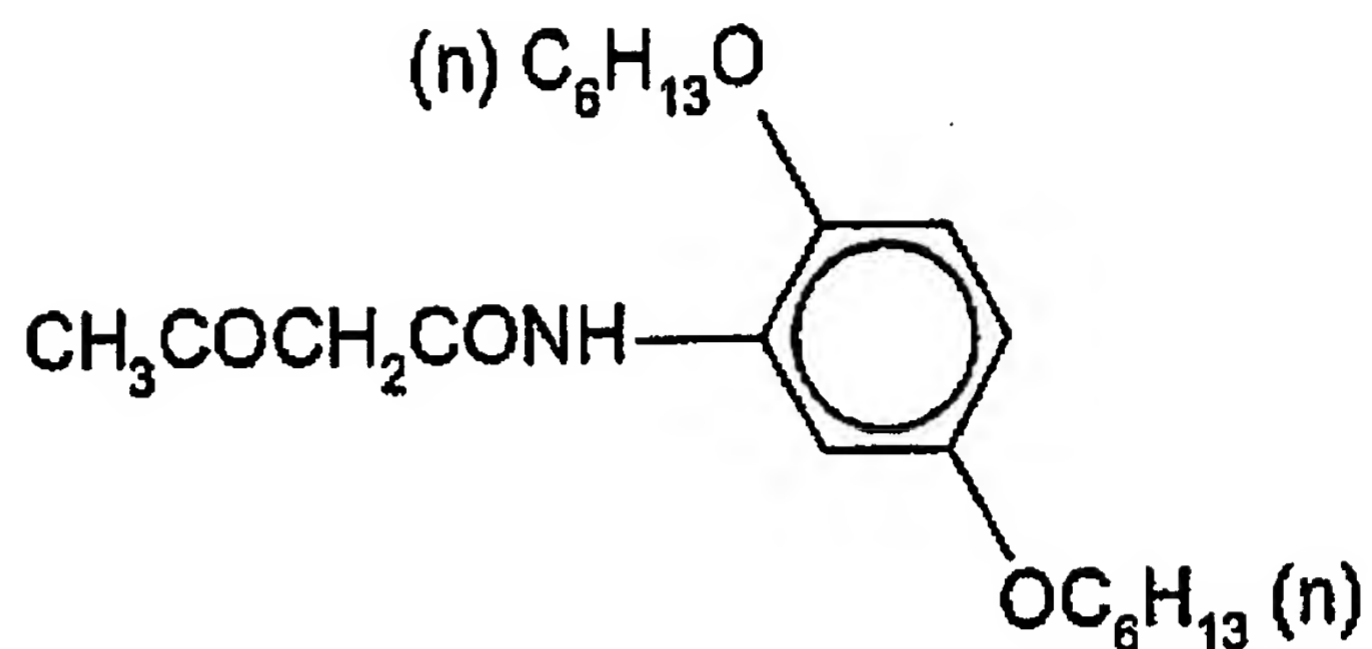


C-4

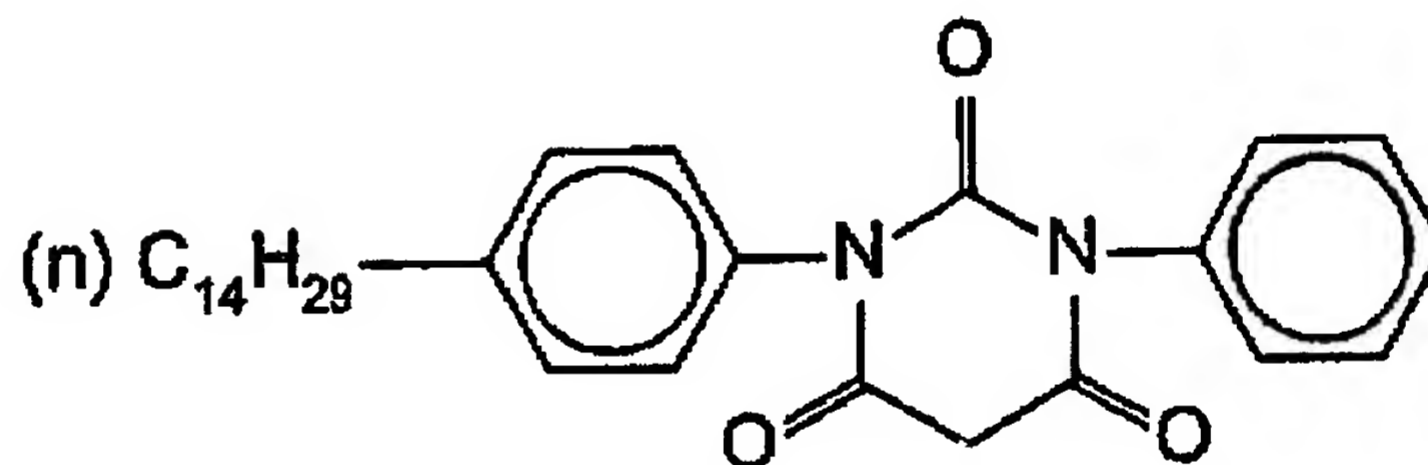


[0058]

C-5



C-6



[0059]

The basic substance is not particularly limited but can be suitably selected from those already known, depending on the purpose, and include not only inorganic and organic basic compounds but also compounds capable of releasing an alkali substance under heating, for example, by decomposition. Representative examples of such alkali-releasing compounds include a nitrogen-containing compound such as an organic ammonium salt, an organic amine, an

amide, urea or thiourea and a derivative thereof, a thiazole, a pyrrole, a pyrimidine, a piperadine, a guanidine, an indol, an imidazole, an imidazoline, a triazole, a morpholine, a piperidine, an amidine, a formazine or a pyridine.

[0060]

Specific examples of such compounds include tricyclohexylamine, tribenzylamine, octadecylbenzylamine, stearylamine, allylurea, thiourea, methylthiourea, allylthiourea, ethylenethiourea, 2-benzylimidazole, 4-phenylimidazole, 2-phenyl-4-methylimidazole, 2-undecylimidazoline, 2,4,5-trifuryl-2-imidazoline, 1,2-diphenyl-4,4-dimethyl-2-imidazoline, 2-phenyl-2-imidazoline, 1,2,3-triphenylguanidine, 1,2-dicyclohexylguanidine, 1,2,3-tricyclohexylguanidine, guanidine trichloroacetic acid salt, N,N'-dibenzylpiperadine, 4,4'-dithiomorpholine, morpholinium trichloroacetic acid salt, 2-aminobenzothiazole, and 2-benzoylhydrazinothiazole. These basic substances may be used singly or in combination of two or more types.

[0061]

The electron donating colorless dye is not particularly limited and can be suitably selected in

accordance with the purpose from those already known. In the invention, an electron donating colorless dye precursor can be employed as the electron donating colorless dye.

[0062]

The electron donating colorless dye precursor can be, for example, a triarylmethane compound, a diphenylmethane compound, a thiazine compound, a xanthene compound or a spiropyran compound. Such compounds may be employed singly or in a combination of two or more types, and, among these compounds, a triarylmethane compound and a xanthene compound are preferred because these compounds are useful in producing high developed color density. Examples of these compounds include 3,3-bis(p-dimethylaminophenyl)-6-dimethylamino phthalide (namely crystal violet lactone), 3,3-bis(p-dimethylamino) phthalide, 3-(p-dimethylaminophenyl)-3-(1,3-dimethylindol-3-yl) phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl) phthalide, 3-(o-methyl-p-diethylaminophenyl)-3-(2-methylindol-3-yl) phthalide, 4,4'-bis(dimethylamino)benzhydrin benzyl ether, N-halophenyl leucoauramin, N-2,4,5-trichlorophenyl leucoauramin, rhodamin-B-anilinolactam, rhodamin(p-nitroanilino) lactam, rhodamin-B-(p-chloroanilino) lactam,

2-benzylamino-6-diethylaminofluoran,
 2-anilino-6-diethylaminofluoran,
 2-anilino-3-methyl-6-diethylaminofluoran,
 2-anilino-3-methyl-6-cyclohexylmethyaminofluoran,
 2-anilino-3-methyl-6-isoamylethylaminofluoran,
 2-(o-chloroanilino)-6-diethylaminofluoran,
 2-octylamino-6-diethylaminofluoran,
 2-ethoxyethylamino-3-chloro-2-diethylaminofluoran,
 2-anilino-3-chloro-6-diethylaminofluoran, benzoyl leuco
 methylene blue, p-nitrobenzyl leuco methylene blue,
 3-methyl-spiro-dinaphthopyran,
 3-ethyl-spiro-dinaphthopyran,
 3,3'-dichloro-spiro-dinaphthopyran,
 3-benzyl-spiro-dinaphthopyran, and 3-propyl-spiro-
 dibenzopyran.

[0063]

The electron accepting compound can be a phenol
 derivative, a salicylic acid derivative or a
 hydroxybenzoic acid ester. For the electron accepting
 compound, particularly preferred are a bisphenol and a
 hydroxybenzoic acid ester. Specific examples of
 particularly preferred electron accepting compounds
 include:

2,2-bis(p-hydroxyphenyl)propane (namely bisphenol-A),

4,4' - (p-phenylenediisopropylidene) diphenol (namely
 bisphenol-P), 2,2-bis(p-hydroxyphenyl)pentane,
 2,2-bis(p-hydroxyphenyl)ethane,
 2,2-bis(p-hydroxyphenyl)butane,
 2,2-bis(4'-hydroxy-3',5'-dichlorophenyl)propane,
 1,1-(p-hydroxyphenyl)cyclohexane,
 1,1-(p-hydroxyphenyl)propane,
 1,1-(p-hydroxyphenyl)pentane,
 1,1-(p-hydroxyphenyl)-2-ethylhexane,
 3,5-di(α -methylbenzyl)salicylic acid and a polyvalent
 metal salt thereof,
 3,5,-di(tert-butyl)salicylic acid and a polyvalent metal
 salt thereof ,
 3- α,α -dimethylbenzylsalicylic acid and a polyvalent metal
 salt thereof, butyl p-hydroxybenzoate, benzyl
 p-hydroxybenzoate, 2-ethylhexyl p-hydroxybenzoate,
 p-phenylphenol and p-cumylphenol.

[0064]

In the present invention, the thermal recording
 layer preferably includes a sensitizer. The sensitizer is
 preferably a low-melting organic compound suitably having
 an aromatic group and a polar group in the molecule.
 Specific examples of the sensitizer include benzyl p-
 benzyloxybenzoate, α -naphthyl benzyl ether, β -naphthyl

benzyl ether, β -naphthoic acid phenyl ester, α -hydroxy- β -naphthoic acid phenyl ester, β -naphthol-(p-chlorobenzyl) ether, 1,4-butanediol phenyl ether, 1,4-butanediol-p-methylphenyl ether, 1,4-butanediol-p-ethylphenyl ether, 1,4-butanediol-m-methylphenyl ether, 1-phenoxy-2-(p-tolyloxy)ethane, 1-phenoxy-2-(p-ethylphenoxy)ethane, 1-phenoxy-2-(p-chlorophenoxy)ethane and p-benzylbiphenyl.

[0065]

Further, the thermal recording layer preferably includes a compound represented by the following general formula (C) in an amount of 0.05 g/m² or higher. In case the thermal recording layer is formed of plural layers, a layer in which the compound represented by the following general formula (C) is included and is not particularly restricted and can be suitably selected according to the purpose. However, the layer is preferably a layer configured by a solid dispersant.

[0066]

General formula (C)



In general formula (C), R represents an alkyl group, an aryl group, an alkoxyl group, an aryloxy group, a polyoxyethylenearyl group or a polyoxyethylenealkyl group.

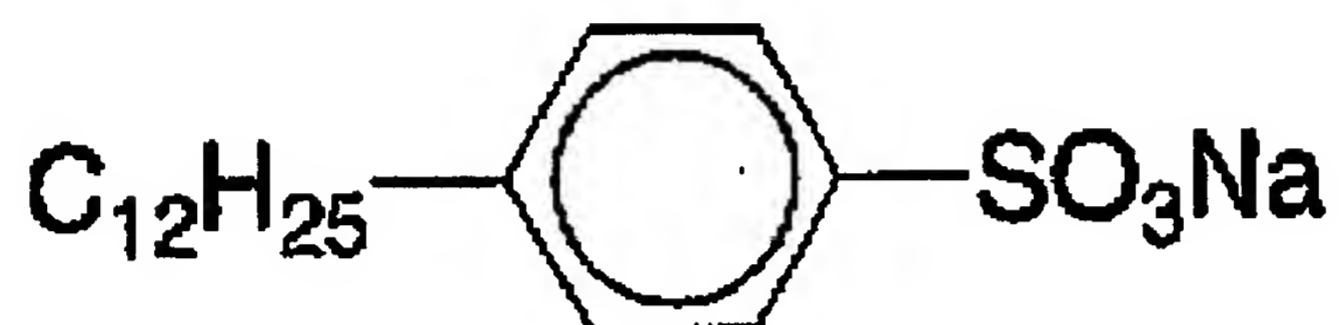
R is preferably an alkyl group with 1 to 20 carbon atoms, an aryl group with 1 to 30 carbon atoms, an alkoxyl group with 1 to 20 carbon atoms, an aryloxy group with 1 to 30 carbon atoms, a polyoxyethylenearyl group with 1 to 30 carbon atoms or a polyoxyethylenealkyl group with 1 to 20 carbon atoms. M represents an alkali metal, which is preferably sodium or potassium.

[0067]

Specific examples of the compound represented by general formula (C) include sodium laurylsulfate, sodium higher alcohol sulfonate, sodium dodecylbenzenesulfonate, sodium alkylnaphthalenesulfonate, sodium dialkylsulfosuccinate, sodium alkyldiphenyl ether disulfonate, sodium polyoxyethylene lauryl ether sulfonate, sodium polyoxyethylene alkyl ether sulfonate, sodium polyoxyethylene alkyl phenyl ether sulfonate, sodium alkanesulfonate, sodium salt of β -naphthalenesulfonic acid-formalin condensate and sodium salt of a specific aromatic sulfonic acid-formalin condensate. The compound represented by general formula (C) may be used singly or in a combination of two or more kinds. In the invention, among these compounds, sodium dodecylbenzenesulfonate represented by the following formula is preferred in order to improve coloration in a

background portion by exposure to light.

[0068]



[0069]

The content of the compound represented by general formula (C) in the thermal recording layer is preferably 0.05 g/m² or higher, more preferably 0.05 to 0.50 g/m² and particularly preferably 0.05 to 0.20 g/m².

A content of less than 0.05 g/m² is not preferable because it may result in insufficient light resistance of the thermal recording material, thus causing background coloration by exposure to light, while on the other hand, a content of equal to or greater than 0.05 g/m² is preferable because it does not encounter such defects and can actually significantly improve the thermal recording material's weather resistance, thereby effectively suppressing background coloration by exposure to light.

[0070]

In the thermal recording layer, the mode of

inclusion of components such as the diazonium salt compound, the coupler capable of color formation by reacting with the diazonium salt compound in a heated state, the basic substance, the electron donating colorless dye, the electron accepting compound, and the sensitizer is not particularly limited but can be suitably selected according to the purpose. For example, these components may be included by (1) a method of inclusion by solid dispersion; (2) a method of inclusion by emulsification; (3) a method of inclusion by polymer dispersion; (4) a method of inclusion by latex dispersion; or (5) a method of inclusion by microencapsulation.

[0071]

Among these methods, the preferred method is inclusion by microencapsulation, in consideration of the storability. When utilizing the color forming reaction of the diazonium salt compound and the coupler, the diazonium salt compound is preferably microencapsulated and included in the thermal recording layer. When utilizing the color forming reaction of the electron donating colorless dye and the electron accepting compound, the electron donating colorless dye is preferably microencapsulated and included in the thermal recording layer.

[0072]

In case the thermal recording layer is constructed with a multi-layered structure, a multi-color thermal recording material can be obtained by employing different color hues in such thermal recording layers. The layer configuration in this case is not particularly restricted and can be suitably selected according to the purpose. In the invention, it is preferable to employ laminated multi-color thermal recording layers, including two thermal recording layers in which two diazonium compounds having different photosensitive wavelengths are respectively combined with couplers capable of forming different color hues by reaction under heating with the respective diazonium salt compounds, and a recording layer in which an electron donating colorless dye and an electron accepting compound are combined. More specifically, it is preferable to use a multi-color thermal recording material in which, on the aforementioned support, are laminated a thermal recording layer A including an electron donating colorless dye and an electron accepting compound; a thermal recording layer B-1 including a diazonium salt compound having a maximum absorption wavelength of 360 ± 20 nm and a coupler capable of forming a color by reaction with the diazonium salt compound under heating; and a thermal recording layer B-2 including a diazonium compound

having a maximum absorption wavelength of 400 ± 20 nm and a coupler capable of forming a color by reaction with the diazonium salt compound under heating, in this order.

[0073]

A recording method using such a multi-color thermal recording material is executed as follows. First, the thermal recording layer B-2 is heated to execute color formation by the diazonium salt compound and the coupler contained in the thermal recording layer B-2. Next, after irradiation with light of a wavelength of 400 ± 20 nm for decomposing the unreacted diazonium salt compound contained in the thermal recording layer B-2, sufficient heat is added for color formation in the thermal recording layer B-1, thereby causing color formation with the diazonium salt compound and the coupler included in the thermal recording layer B-1. At the same time, the thermal recording layer B-2 is also strongly heated, but no further color formation takes place because the diazonium salt compound is already decomposed and color forming ability is lost. Next, irradiation with light of a wavelength of 360 ± 20 nm is executed for decomposing the diazonium salt compound included in the thermal recording layer B-1, and lastly, sufficient heat is added for color formation in thermal recording layer A, thereby

forming a color therein. At the same time, the thermal recording layers B-2 and B-1 are also strongly heated, but no further color formation takes place because the diazonium salt compounds are already decomposed and the color forming ability is lost.

[0074]

In the present invention, it is also preferable to employ laminated multi-color thermal recording layers, including three thermal recording layers in which three diazonium salt compounds having different photosensitive wavelengths are respectively combined with couplers capable of forming different color hues by reaction under heating with the respective diazonium salt compounds. It is preferable to use a multi-color thermal recording material in which are laminated, on the aforementioned support, a thermal recording layer A-1 including a diazonium salt compound having a maximum absorption wavelength of 350 nm or less, and preferably of 340 nm or less, and a coupler capable of forming a color by reaction under heating with the diazonium salt compound; a thermal recording layer A-2 including a diazonium salt compound having a maximum absorption wavelength of 360 ± 20 nm and a coupler capable of forming a color by reaction under heating with the diazonium salt compound; and a thermal

recording layer A-3 including a diazonium salt compound having a maximum absorption wavelength of 400 ± 20 nm and a coupler capable of forming a color by reaction under heating with the diazonium salt compound, in this order.

In such multi-color thermal recording layers, full-color image recording is possible by selecting three primary colors in the subtractive color mixing, namely yellow, magenta and cyan, for the color hues to be formed in these recording layers.

[0075]

<Support>

The aforementioned support can be, for example, a polyester film such as of polyethylene terephthalate or polybutylene terephthalate; a cellulose derivative film such as a cellulose triacetate film; a polyolefin film such as a polystyrene film, a polypropylene film or a polyethylene film; a plastic film such as a polyimide film, a polyvinyl chloride film, a polyvinylidene chloride film, an acrylic acid copolymer film or a polycarbonate film; paper, synthetic paper or paper having a plastic resin layer, and it is preferred to use a support having a layer made of one of the above-mentioned plastic films. Such a support may be transparent or opaque, and may be used singly or in combination of two or more kinds.

[0076]

It is advantageous for such a support having the plastic layer to be a base paper having, on either both surfaces or at least one surface where the recording layer is to be formed, a layer formed by a thermoplastic resin. Such a support can be, for example, (1) a base paper on which a thermoplastic resin is coated by melt extrusion; (2) a base paper having a melt-extruded thermoplastic resin on which a gas barrier layer is coated; (3) a base paper adhered to a plastic film of low oxygen permeability; (4) a base paper adhered to a plastic film on which a thermoplastic resin is coated by melt extrusion; or (5) a base paper coated with a thermoplastic resin by melt extrusion, and then adhered to a plastic film.

[0077]

The thermoplastic resin to be melt extrusion coated on the base paper can advantageously be an olefinic polymer, for example, a single polymer of alpha-olefin such as polyethylene or polypropylene or a mixture of such polymers, or a random copolymer of ethylene and vinyl alcohol. The polyethylene mentioned above can be, for example, low density polyethylene (LDPE), high density



polyethylene (HDPE), or linear low density polyethylene (L-LDPE).

[0078]

The method of adhering the plastic film to the base paper is not particularly limited, and can be suitably selected from known lamination methods such as those described in *Shin-laminate Kako Binran* (New Lamination Work Handbook) edited by Kako Gijutsu Kenkyukai. Advantageous examples include so-called dry lamination, solventless dry lamination, dry lamination utilizing an electron beam- or ultraviolet-curable resin, or hot dry lamination.

Among the supports mentioned in the foregoing, it is particularly preferable in the present invention to use a base paper formed from natural pulp as the main component and which has an olefinic polymer coating on both surfaces.

[0079]

<Undercoat layer>

In the invention, an undercoat layer is preferably provided between the support and the thermal recording layer.

The undercoat layer is not particularly restricted,

and can be suitably selected from known layers, according to the purpose. The undercoat layer particularly preferably includes gelatin having a PAGO method viscosity of 10 to 30 mP and a PAGO method jelly strength of 15 to 70 g (hereinafter, simply referred to as "gelatin") and a layered inorganic compound. In the invention, it is also preferred that the above-described layer be provided as an intermediate layer or the like, and will be explained later.

[0080]

The PAGO method viscosity and the PAGO method jelly strength are measured by a test based on *PAGO Method: Test Methods for Photographic Gelatin*; 7th edition (1992); published by the United Association for Photographic Gelatin Test Method.

The above-mentioned gelatin is obtained by reducing the molecular weight of a known gelatin produced by an ordinary method (hereinafter referred to as "ordinary gelatin"). The ordinary gelatin mentioned above is produced by processing a raw material such as cow bone, cow hide or pig hide with lime or an acid, as described in *Glue and Gelatin*, edited by Yoshihiro Abiko, Japan Glue and Gelatin Industry Association (1987), and has a viscosity and a jelly strength far greater than those of

the aforementioned gelatin.

[0081]

Ordinary gelatin is characterized by conditions such as the raw materials used, the processing method (e.g., lime processing or acid processing), and extracting conditions (e.g., temperature, number of extractions, etc.). The aforementioned gelatin may be obtained by molecular weight reduction from any gelatin. However, it is preferable to use a gelatin extracted with a fewer number of extractions and at a lower temperature, in order to simultaneously attain low viscosity and jelly strength within the aforementioned ranges.

For the molecular weight reduction method, a method of employing an enzyme or a method of utilizing heat can be employed. Among these methods, the method employing an enzyme is preferred. In the method of utilizing heat, the jelly strength may become low when the viscosity is lowered to the desired value. An example of an enzyme includes papain, which can be advantageously employed.

[0082]

The aforementioned gelatin has a PAGI method viscosity of 10 to 30 mP and a PAGI method jelly strength of 15 to 70 g. A PAGI method viscosity of less than 10 mP

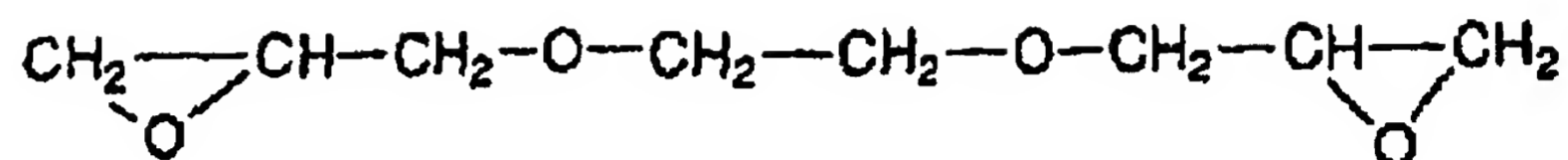
may cause a large reduction of viscosity in the coating solution, thereby possibly deteriorating a dispersed state of a pigment (mica) in the coating solution, while a viscosity exceeding 30 mP elevates the viscosity of the coating solution, thereby resulting in coating defects. Also a PAGI method jelly strength of less than 15 g lowers a coated film strength, thereby resulting in lowered adhesion strength with the support, while a jelly strength exceeding 70 g may increase curling of the coated film by changes in environmental conditions.

[0083]

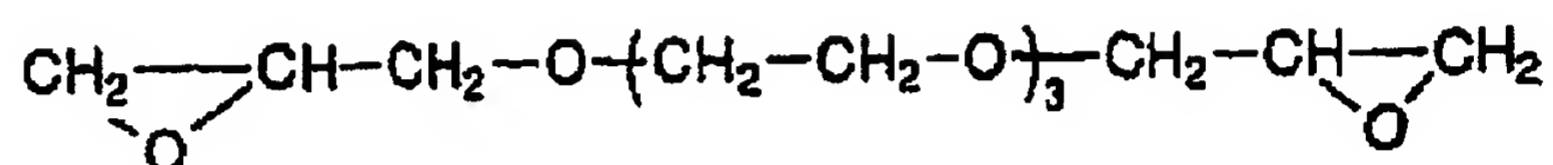
The aforementioned gelatin may be crosslinked with a hardening agent if necessary. In such a case, a known hardening agent may be employed for the gelatin. Examples of such known hardening agents include a vinylsulfone compound, an active halogen compound, an isocyanate compound, and an epoxy compound. Among these, use of an epoxy compound is particularly preferred, and preferred examples of such epoxy compounds are shown below:

[0084]

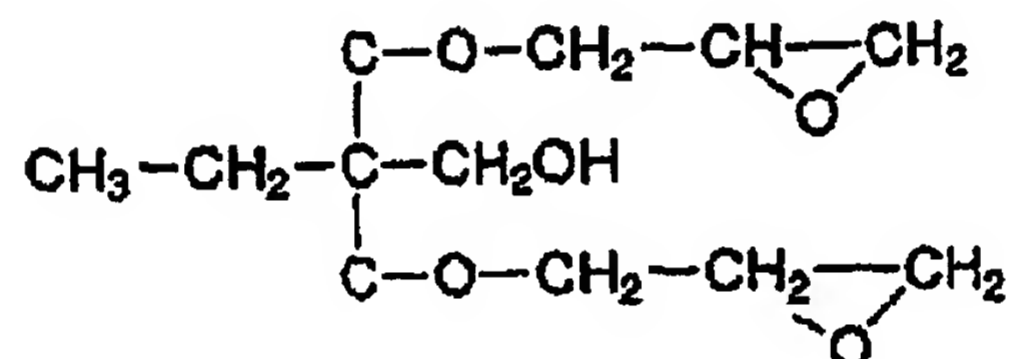
E - 1



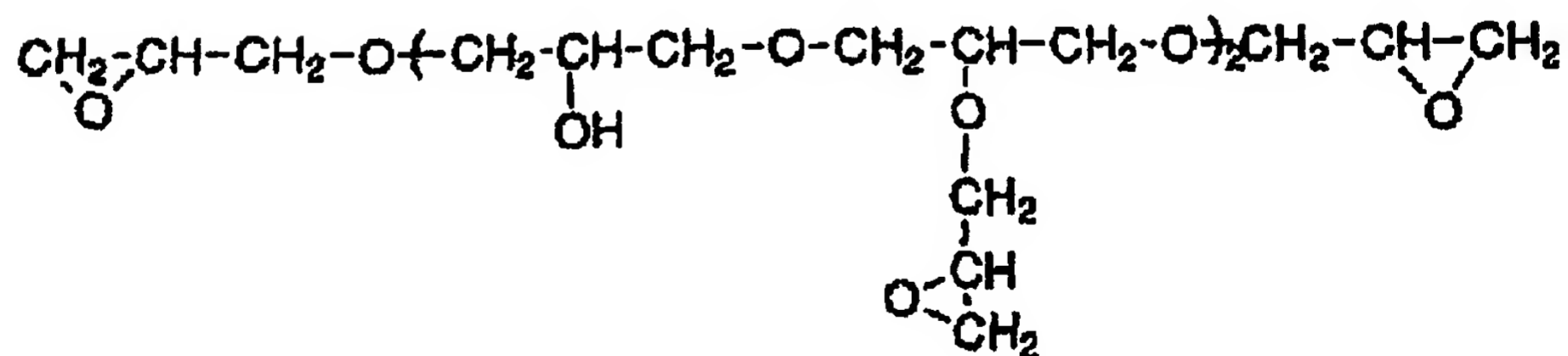
E - 2



E - 3



E - 4



[0085]

A coating amount of the gelatin in the undercoat layer is preferably 0.5 g/m² or higher, in view of suppressing blisters (small swellings formed by the heat of the thermal head of the printer during printing).

[0086]

A swelling inorganic layered compound can be advantageously employed as the aforementioned layered inorganic compound. Specific examples of such swelling inorganic layered compounds include a swelling clay mineral such as bentonite, hectorite, saponite, biedellite, nontronite, stevensite, beidellite or montmorillonite, swelling synthetic mica, and swelling synthetic smectite.

[0087]

Such swelling inorganic compounds have a layered structure constituted by a unit crystal lattice layer of a thickness of about 10 to 15 Angstroms, and shows significantly larger in-lattice metal atom substitutions than other clay minerals. As a result, the lattice layer generates a deficiency in a positive charge, and cations such as Na^+ , Ca^{2+} or Mg^{2+} are adsorbed between the layers in order to compensate such charge deficiency. Such cations present between the layers are called "exchangeable cations", which can be exchanged with various cations. When these interlayer cations are Li^+ , Na^+ etc., because of the small ionic radius thereof, the bond between the layered crystal lattices is weak and water causes large

swelling. When a shearing force is applied to the crystal in such a state, the crystal is easily cleaved to form a stable sol in water. Among the aforementioned specific examples of the swelling inorganic layered compounds, bentonite and swelling synthetic mica are preferred because they tend to cause the above-described phenomenon, and the swelling synthetic mica is particularly preferred.

[0088]

Preferred examples of swelling synthetic mica include:

Na tetrasic mica $\text{NaMg}_{2.5}(\text{Si}_4\text{O}_{10})\text{F}_2$,
Na/Li teniolite $(\text{NaLi})\text{Mg}_2(\text{Si}_4\text{O}_{10})\text{F}_2$, and
Na/Li hectorite $(\text{NaLi})_{1/3}\text{Mg}_{2/3}\text{Li}_{1/3}(\text{Si}_4\text{O}_{10})\text{F}_2$.

[0089]

The swelling synthetic mica generally has a thickness of 1 to 50 nm and a flat plane size of 1 to 20 μm . The thickness is preferably as small as possible for diffusion control, and the flat plane size is preferably as large as possible, as long as it does not exceed the extent where it would deteriorate the smoothness and transparency of the coated surface. The swelling synthetic mica usually has an aspect ratio of 100 or larger, preferably 200 or larger and more preferably 500

or larger.

[0090]

In case of employing the aforementioned ordinary gelatin, when the ratio of the mica is increased (1.5 - 10% or higher to gelatin), viscosity increases and gelation at a constant solid concentration accelerates (e.g., 5 to 10%), so that reduction of the viscosity becomes necessary. In order to reduce the gelatin viscosity, a method of decreasing the concentration may be adopted, but reduction in the concentration increases a drying load for the coated film, eventually resulting in a deteriorated surface condition by thicker coating.

Also, there is known a method of adding urea or a salt to the coating solution, but such methods cannot attain sufficient reduction of the viscosity and cannot provide satisfactory surface state after coating. In contrast, the aforementioned gelatin is free from such drawbacks and is advantageous in significantly reducing the viscosity increase and the gelation, even when mica is used in combination.

[0091]

A content of the water swelling synthetic mica in the undercoat layer is preferably $1/20$ to $1/2$ in a

mica/gelatin mass ratio.

With the content of the water swelling synthetic mica less than $1/20$, the undercoat layer can satisfactorily function as an oxygen intercepting layer, and can also prevent deterioration of manufacturing properties such as a coating property in case that the content exceeds $1/2$.

[0092]

In the undercoat layer, the coating amount of the mica is usually 0.01 g/m^2 or higher, preferably 0.02 g/m^2 or higher. With the coating amount of the mica less than 0.01 g/m^2 , the mica lowers oxygen intercepting ability in the undercoat layer and can not exhibit a property of preventing coloration in the background portion.

[0093]

<Light transmittance control layer>

In the thermal recording material of the invention, a light transmittance control layer is preferably provided in order to improve light fastness.

The light transmittance control layer may include an ultraviolet absorber precursor, which does not function as an ultraviolet absorber prior to irradiation with light of a wavelength region required for fixation of a photo-

fixable thermal recording layer, hence the layer shows a high optical transmittance. Also at the fixation of the photo-fixable thermal recording layer, the light transmittance control layer sufficiently transmits the light of the wavelength region required for fixation, and also shows a high light transmittance in the visible region, thereby not hindering the fixation of the thermal recording layer. This ultraviolet absorber precursor is preferably included in microcapsules. The compound to be included in the light transmittance control layer can be those described in JP-A No. 9-1928.

[0094]

After irradiation with light of the wavelength region required for the fixation of the thermal recording layer by light irradiation, the ultraviolet absorber precursor is reacted by light or heat to become functionable as an ultraviolet absorber. Most of the light of the ultraviolet wavelength region required for the fixation is absorbed by the ultraviolet absorber, whereby the transmittance is lowered. Therefore the light fastness of the thermal recording material is improved, but the transmittance for visible light remains substantially unchanged because the ultraviolet absorber lacks an absorbing effect for visible light.

The light transmittance control layer can be provided in at least one layer in the thermal recording material. It is most preferably provided between a thermal recording layer and an outermost protective layer. The light transmittance control layer may also be constructed so as to serve as a protective layer. Characteristics of the light transmittance control layer can be arbitrarily selected according to the characteristics of the thermal recording layer.

[0095]

The coating solution for forming the light transmittance control layer (light transmittance control layer coating solution) can be obtained by mixing the components explained in above. The light transmittance control layer can be formed by coating the thus-obtained coating solution with a known coating method such as bar coating, air knife coating, blade coating or curtain coating. The light transmittance control layer may be coated simultaneously with the thermal recording layer, or coated and formed on the thermal recording layer after the coating solution for forming the thermal recording layer is coated and dried.

The dry coating amount of the light transmittance control layer is preferably within a range of 0.8 to 4.0

g/m².

[0096]

<Intermediate layer>

When superposing multiple thermal recording layers, an intermediate layer is preferably provided between the thermal recording layers. The intermediate layer may contain, as in the protective layer, various binders, a pigment, a lubricant, a surfactant, a dispersant, a fluorescent whitening agent, a metal soap, an ultraviolet absorber, etc. The binder can be similar to those used in the protective layer. Also, in order to increase the film strength of the thermal recording material, a hardening agent such as a crosslinking agent such as boric acid capable of causing a crosslinking reaction with the binder of the protective layer can be added in a coating solution for the intermediate layer.

[0097]

The thermal recording layer, the protective layer, the light transmittance control layer, the intermediate layer, etc. can be formed, on a support, by coating and drying with known coating methods such as blade coating, air knife coating, gravure coating, roll coating, spray coating, dip coating or bar coating.

[0098]

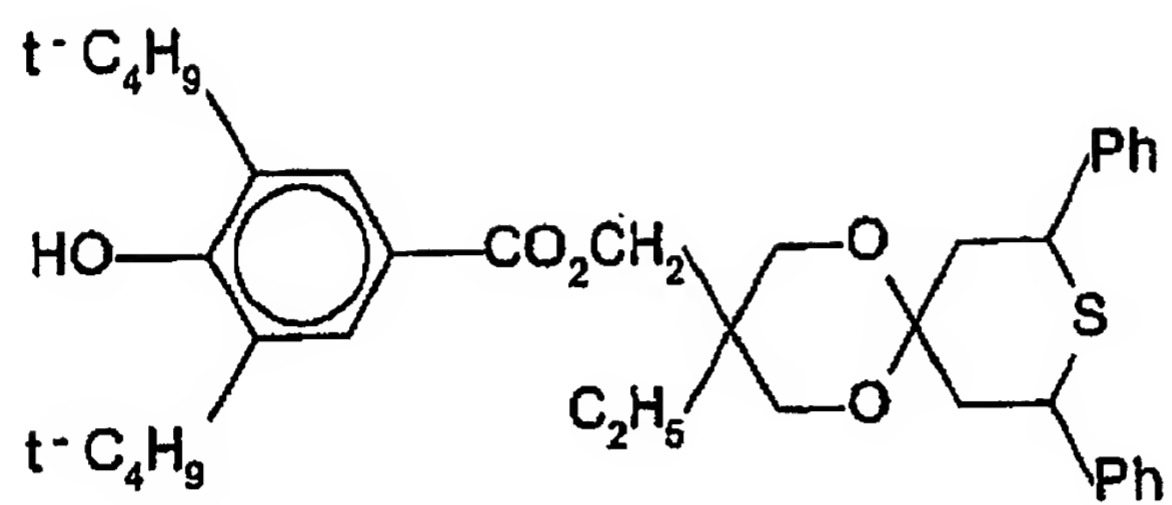
(Antioxidant)

In the invention, in order to further improve light fastness, known antioxidants as shown in the following patent documents may be added to the thermal recording material.

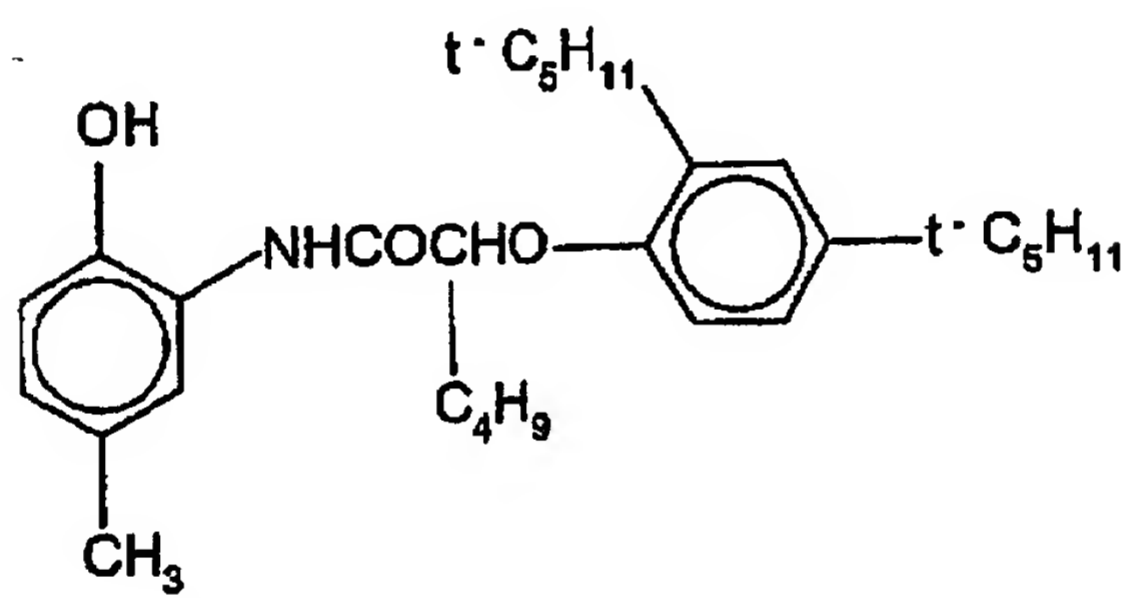
Examples of such antioxidants include those described in EP-A No. 310551, GP-A No. 3435443, EP-A No. 310552, JP-A No. 3-121449, EP-A No. 459416, JP-A Nos. 2-262654, 2-71262 and 63-163351, USP No. 4,814,262, JP-A Nos. 54-48535, 5-61166 and 5-119449, USP No. 4,980,275, JP-A Nos. 63-113536 and 62-262047, EP-A Nos. 223739, 309402 and 309401. Specific examples of the antioxidant are shown below.

[0099]

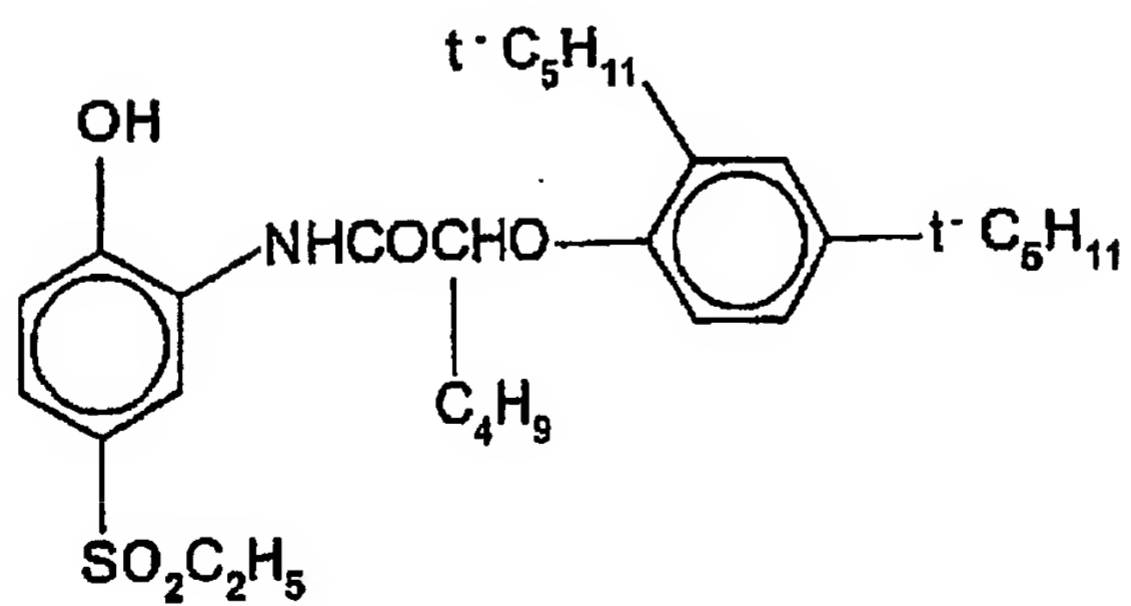
Q-1



Q-2

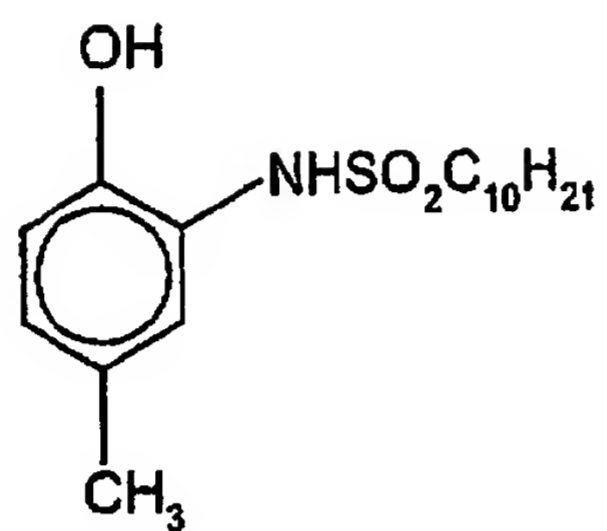


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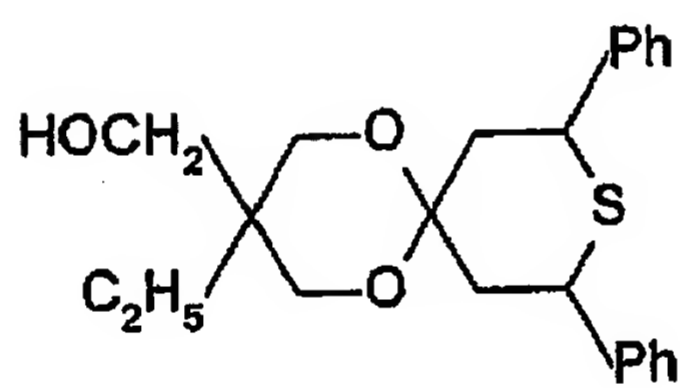


[0100]

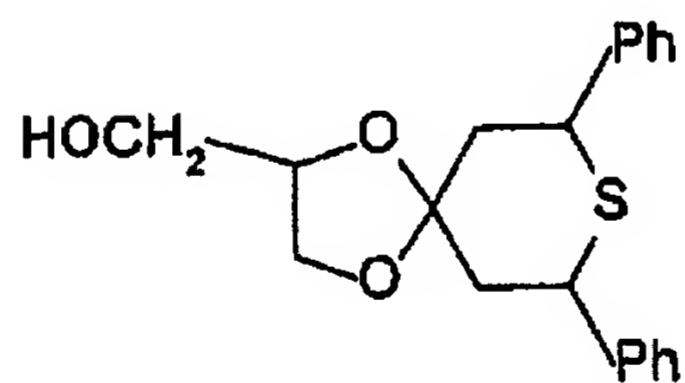
Q-4



Q-5

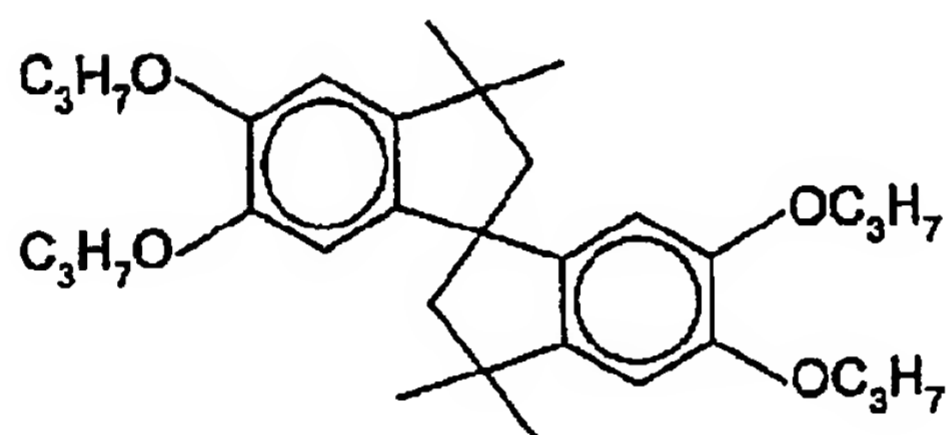
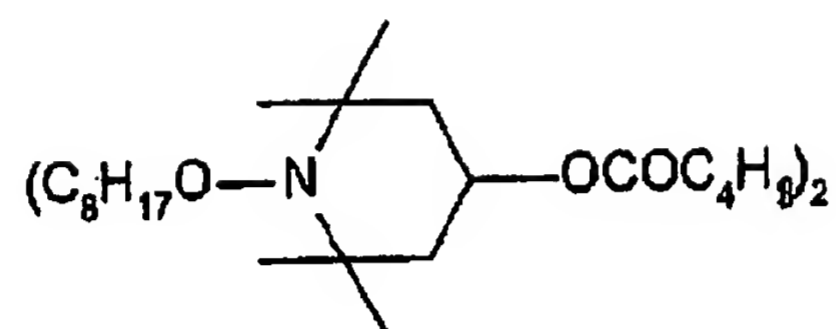


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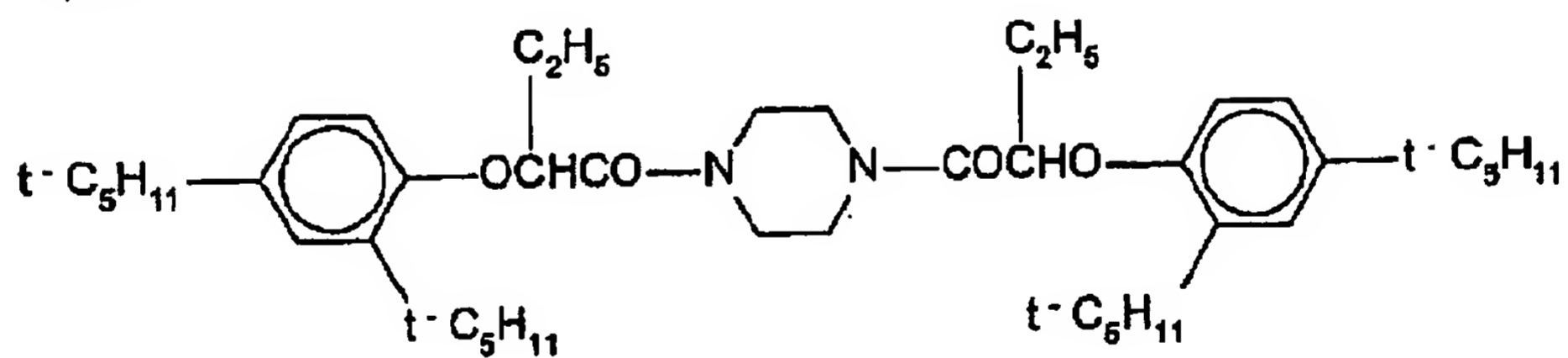


[0101]

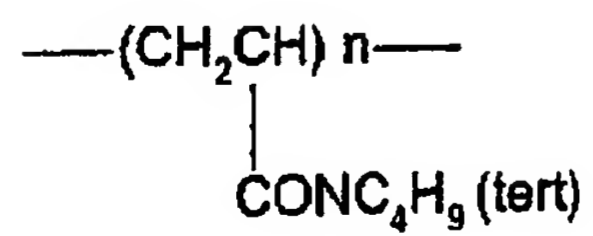
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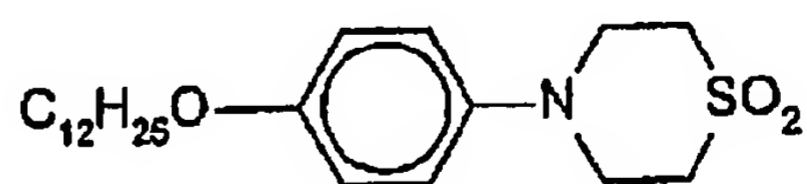
Q-8



Q-9

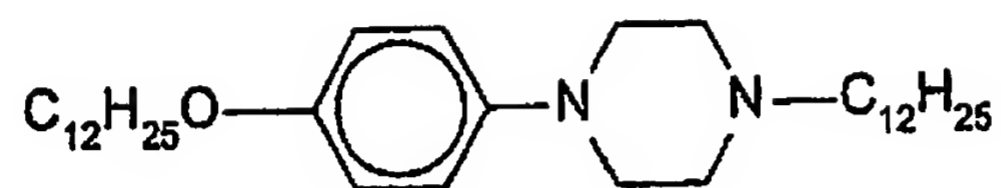


Q-10

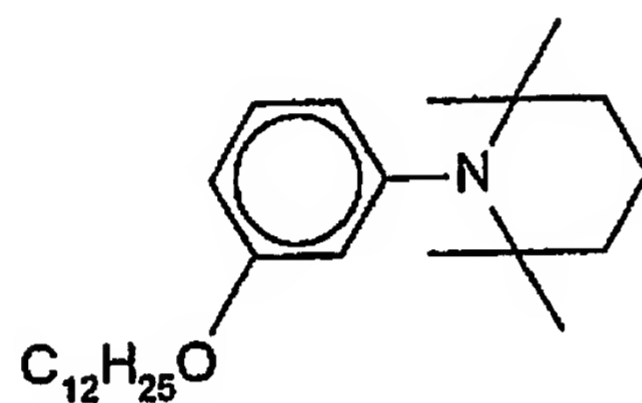


[0102]

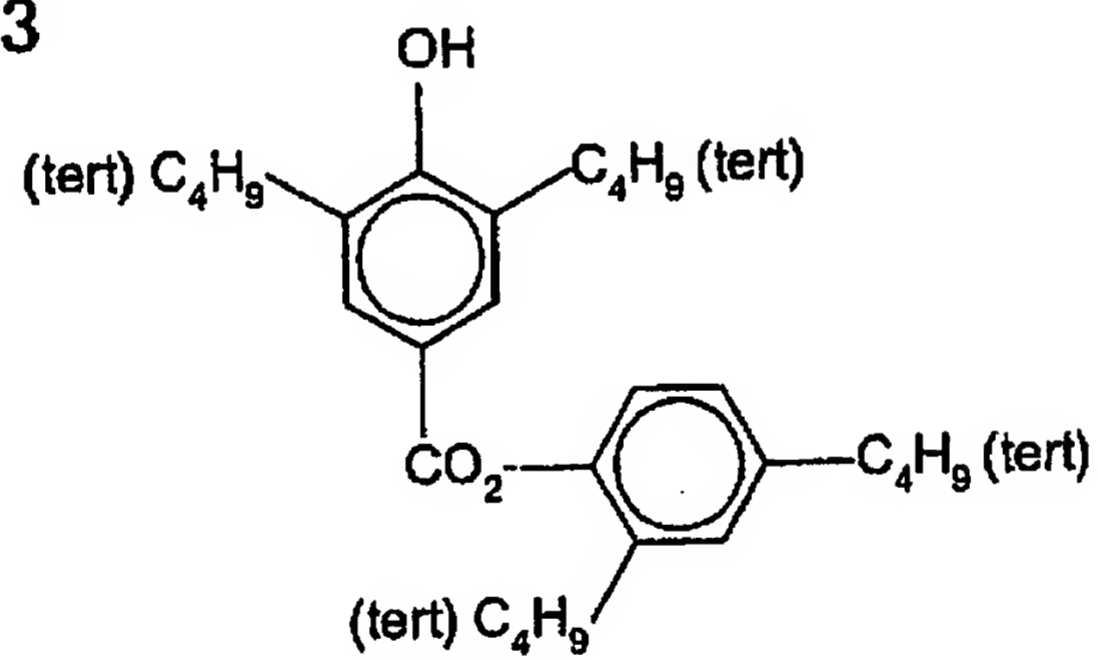
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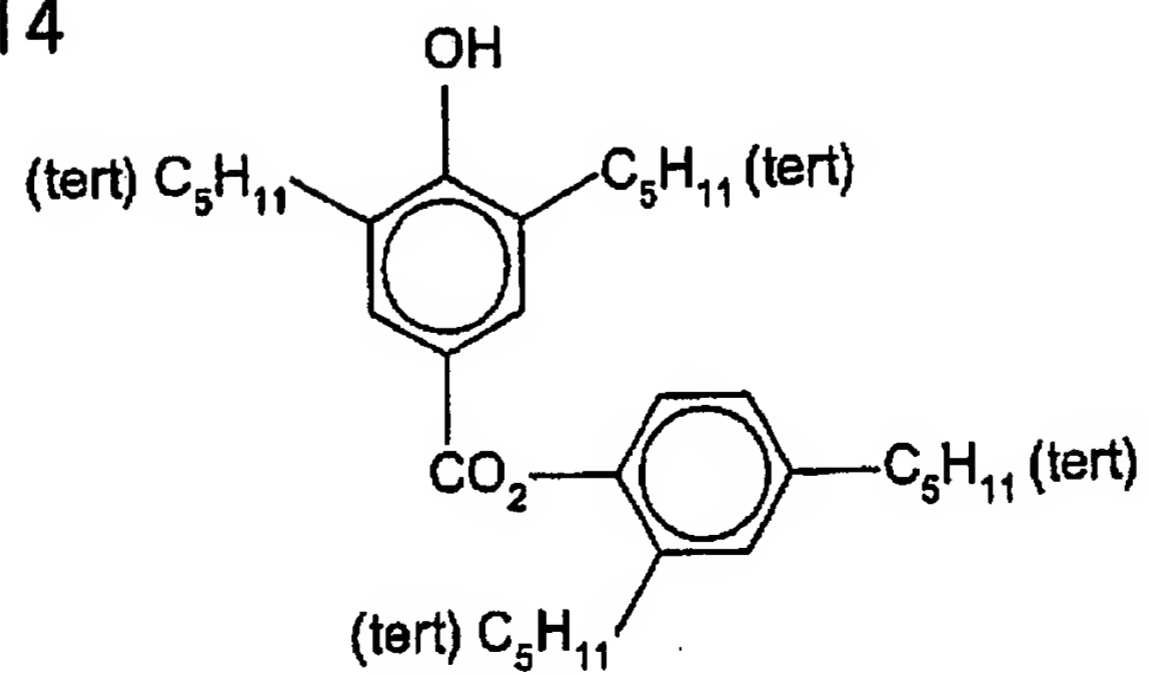
Q-12



Q-13

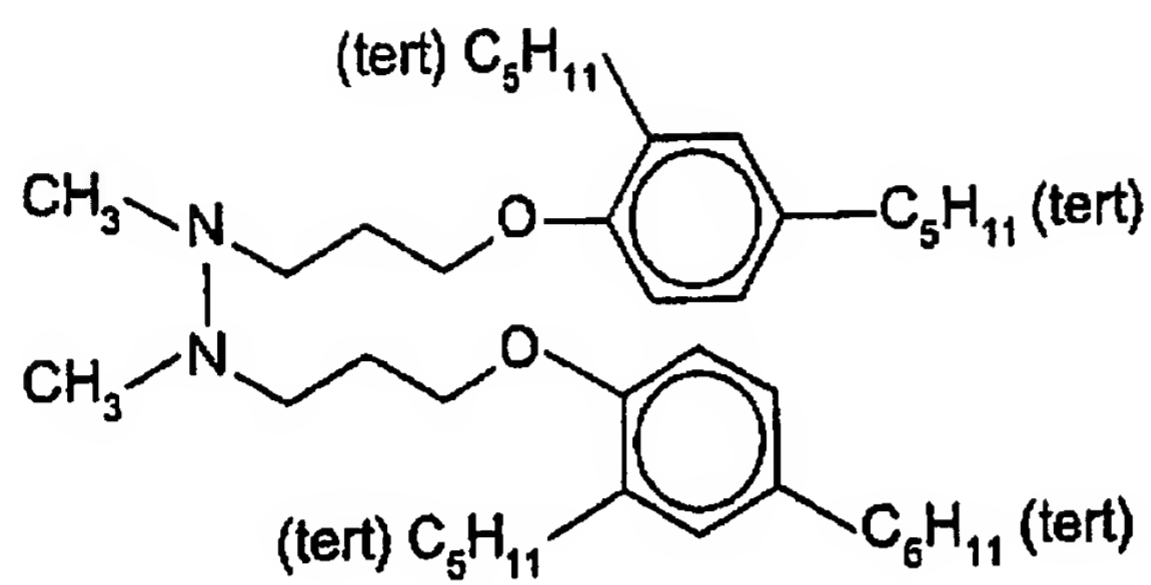


Q-14

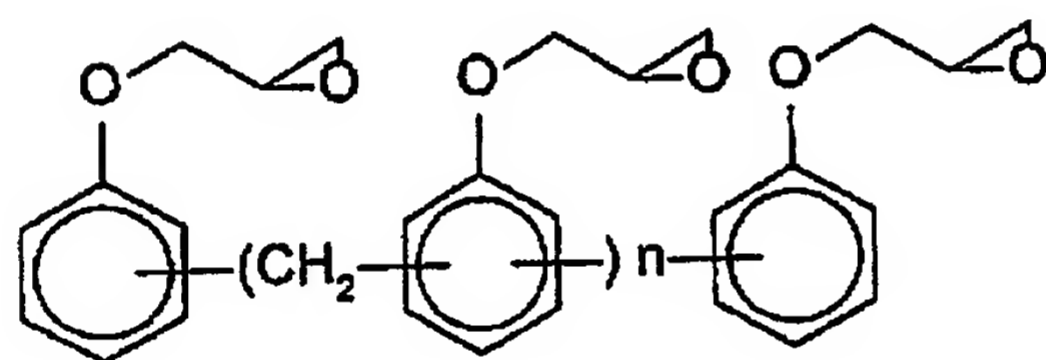


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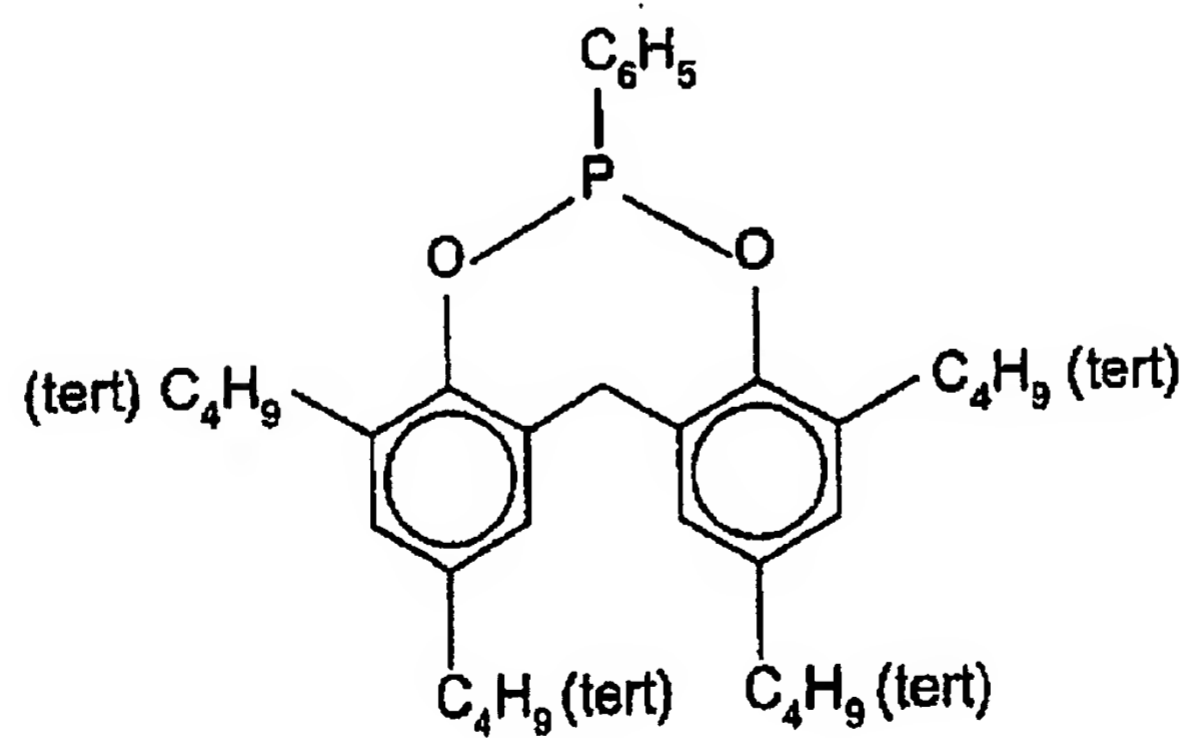
Q-15



Q-16

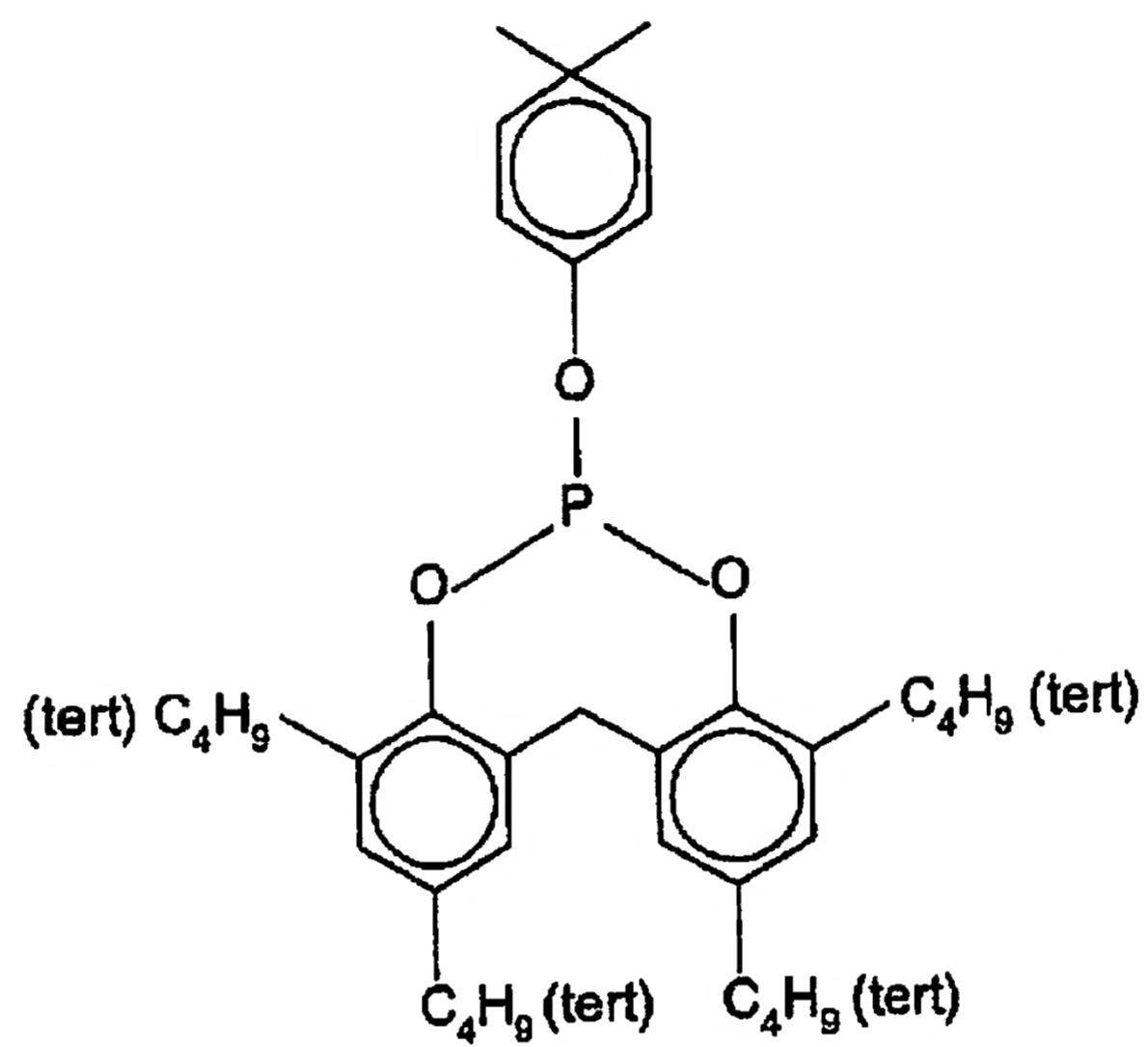


Q-17



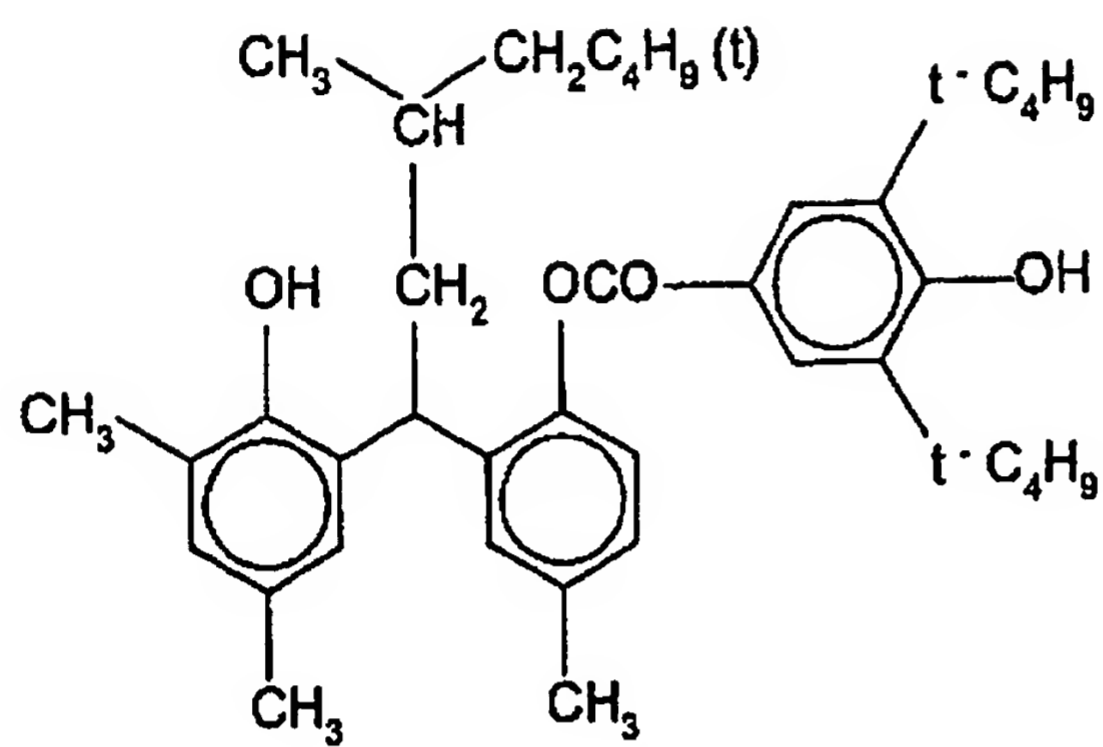
[0104]

Q-18

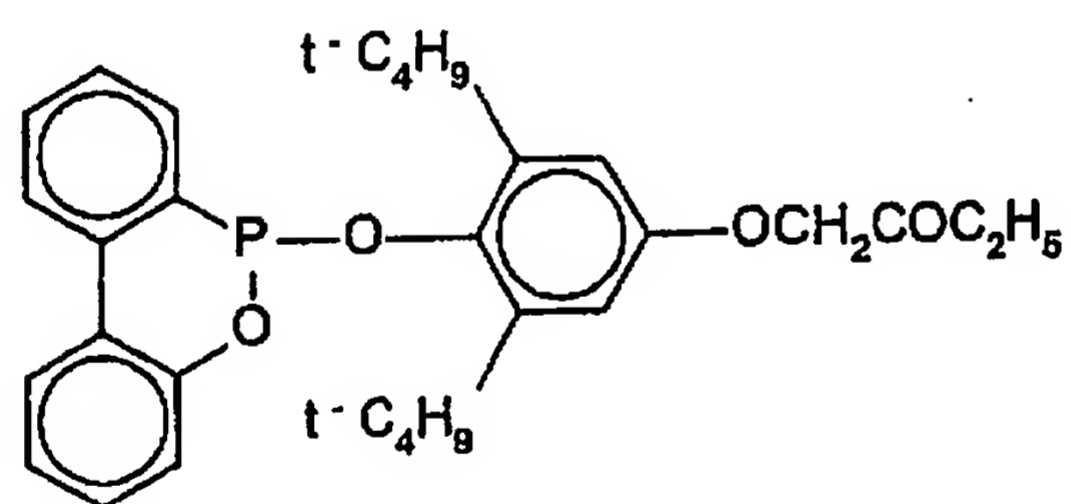


[0105]

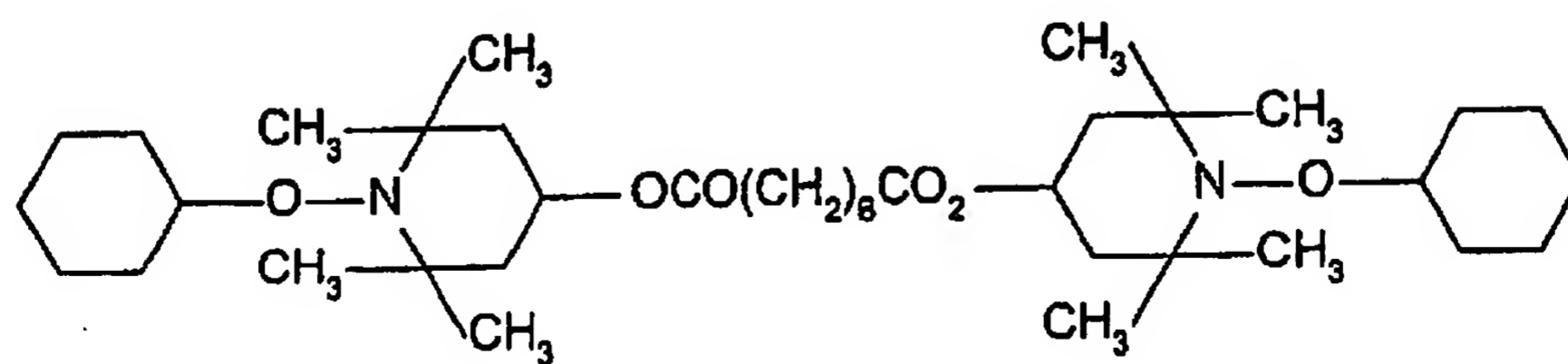
Q-19



Q-20

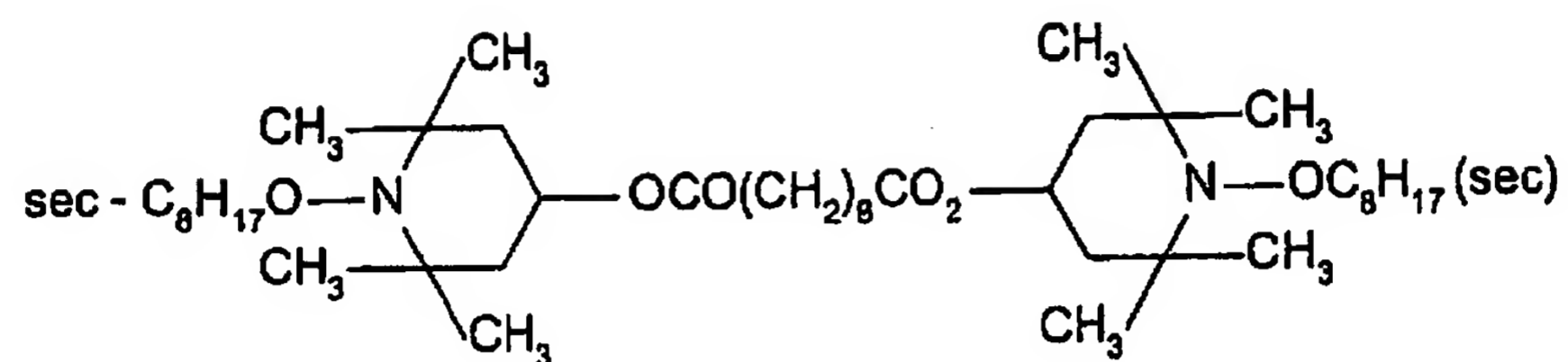


Q-21

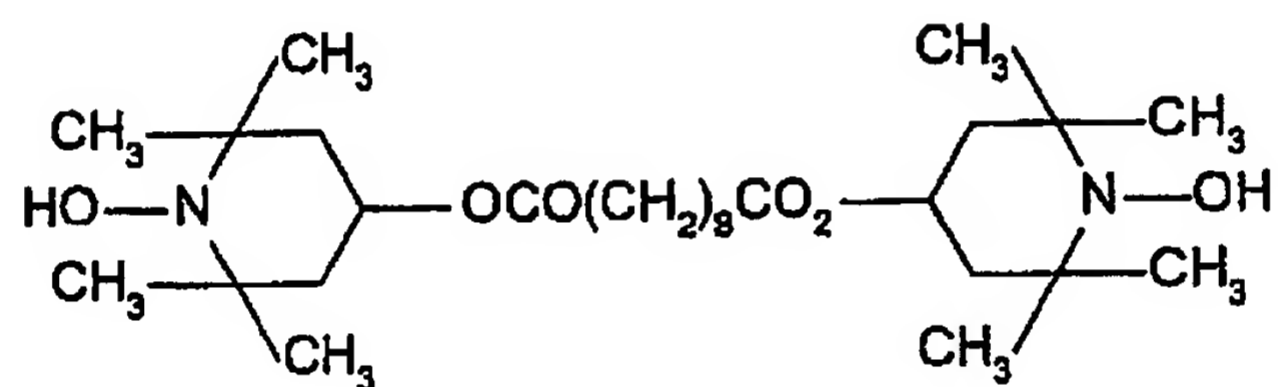


[0106]

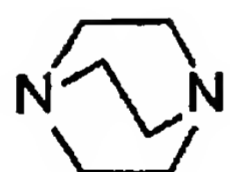
Q-22



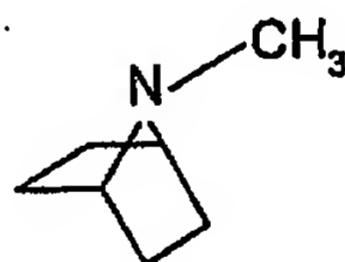
Q-23



Q-24



Q-25



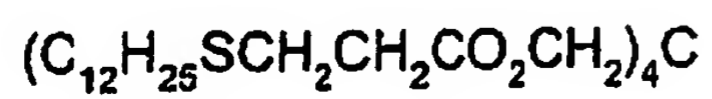
Q-26



Q-27



Q-28



[0107]

Examples of the antioxidant include those described in JP-A Nos. 60-125470, 60-125471, 60-125472, 60-287485, 60-287486, 60-287487, 62-146680, 60-287488, 62-282885, 63-89877, 63-88380, 63-088381, 01-239282, 04-291685, 04-291684, 05-188687, 05-188686, 05-110490, 05-1108437, 05-170361, 63-203372, 63-224989, 63-267594, 63-182484, 60-107384, 60-107383, 61-160287, 61-185483, 61-211079, 63-251282 and 63-051174, JP-B Nos. 48-043294 and 48-033212.

[0108]

Specific examples of the antioxidant include 6-ethoxy-1-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-1-octyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-1-phenyl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline, 6-ethoxy-1-octyl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline, nickel cyclohexanate, 2,2-bis-4-hydroxyphenylpropane, 1,1-bis-4-hydroxyphenyl-2-ethylhexane, 2-methyl-4-methoxy-diphenylamine, and 1-methyl-2-phenylindole.

Such antioxidant may be added in the thermal recording layer, the intermediate layer, the light

transmittance control layer or in the protective layer.

[0109]

[EXAMPLES]

Below, examples of the present invention will be explained, but the invention is not limited by such examples. In the following description, "part" means "part by mass", unless otherwise specified.

[0110]

[Example 1]

<Preparation of phthalated gelatin aqueous solution>

32 parts of phthalated gelatin (trade name: MGP gelatin, manufactured by Nippi Collagen Co., Ltd.); 0.7 parts of 1,2-benzothiazolin-3-one (3.5% methanol solution, manufactured by Daito Chemical Industries, Ltd.); and 367.1 parts of ion-exchanged water were mixed and dissolved at 40°C to obtain a phthalated gelatin aqueous solution.

[0111]

<Preparation of alkali-treated aqueous gelatin solution>

25.5 parts of alkali-treated low-ion content gelatin (trade name: #750 gelatin, manufactured by Nitta Gelatin Inc.); 0.6 parts of 1,2-benzothiazolin-3-one (3.5%

methanol solution, manufactured by Daito Chemical Industries, Ltd.); 0.153 parts of calcium hydroxide and 143.6 parts of ion-exchanged water were mixed and dissolved at 50°C to obtain an alkali-treated gelatin aqueous solution for preparing an emulsion.

[0112]

(1) Preparation of coating solution for yellow thermal recording layer (a)

<Preparation of microcapsule solution (a) including diazonium salt compound>

To 16.1 parts of ethyl acetate, 3.2 parts of a following diazonium compound (A) (maximum absorption wavelength 420 nm); 1.2 parts of a following diazonium compound (B) (maximum absorption wavelength 420 nm); 4.8 parts of monoisopropylbiphenyl; 4.8 parts of diphenyl phthalate; and 0.4 parts of diphenyl-(2,4,6-trimethylbenzoyl)phosphin oxide (trade name: Lucirin TPO, manufactured by BASF Japan Ltd.) were added and dissolved uniformly by heating at 40°C. To the thus-obtained mixture, 8.6 parts of a mixture of xylylene diisocyanate/trimethylolpropane adduct and xylylene diisocyanate/bisphenol-A adduct (trade name: Takenate D119N (50% solution in ethyl acetate), manufactured by Mitsui-Takeda Chemicals, Inc.) were added as a capsule

wall material and were uniformly stirred to obtain a mixture (I).

[0113]

Separately, 58.6 parts of the above-mentioned phthalated gelatin aqueous solution were added with 16.3 parts of ion-exchanged water and 0.34 parts of Scrapp AG-8 manufactured by Nippon Seika Co. to obtain a mixture (II).

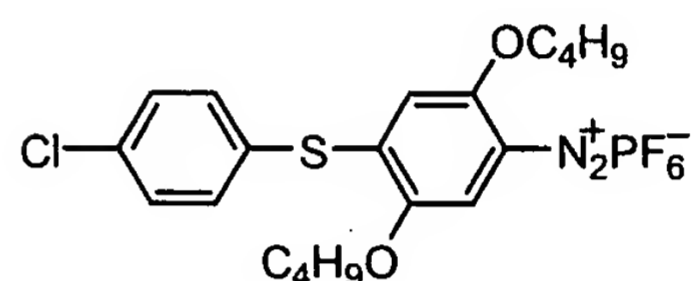
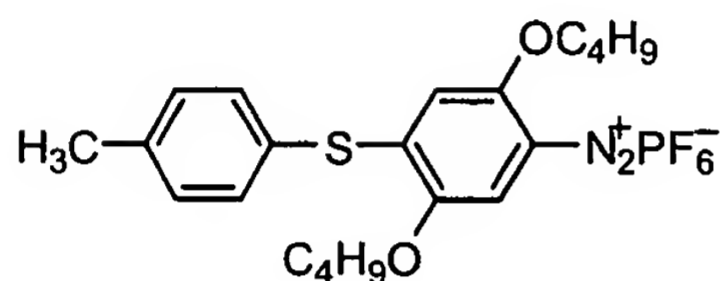
Mixture (I) was added to mixture (II), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion was added and mixed uniformly with 20 parts of water, and was subjected to an encapsulation reaction for 3 hours while stirring at 40°C and eliminating the ethyl acetate. Next, 4.1 parts of an ion exchange resin (trade name: Amberlite IRA68, manufactured by Organo Corp.) and 8.2 parts of an ion exchange resin (trade name: Amberlite IRC50, manufactured by Organo Corp.) were added and the mixture was further stirred for 1 hour. Thereafter, the ion exchange resin was eliminated by filtration, and the capsule solution was subjected to an adjustment of concentration so as to obtain a solid content of 20.0%, thereby obtaining a microcapsule solution (a) including the diazonium salt compound. The result of measurement with a particle size measurement apparatus (trade name:

LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of 0.36 μm .

[0114]

Diazonium compound (A)

Diazonium compound (B)



[0115]

<Preparation of coupler compound emulsion (a)>

7.7 parts of a following coupler compound (C); 9.9 parts of triphenylguanidine (manufactured by Hodogaya Chemical Co., Ltd.); 20.8 parts of 4,4'-(m-phenylenediisopropylidene)-diphenol (trade name: Bisphenol M, manufactured by Mitsui Chemicals Inc.); 3.3 parts of 3,3,3',3'-tetramethyl-5,5',6,6'-tetra(1-propyloxy)-1,1'-spirobisindane; 13.6 parts of 4-(2-ethylhexyloxy)benzenesulfonic acid amide (manufactured by Manac Incorporated.); 6.8 parts of 4-n-pentyloxybenzenesulfonic acid amide (manufactured by Manac Incorporated); and 4.2 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C (70% methanol solution), manufactured by Takemoto Oil & Fat

Co., Ltd) were dissolved in 33.0 parts of ethyl acetate to obtain a mixture (III).

[0116]

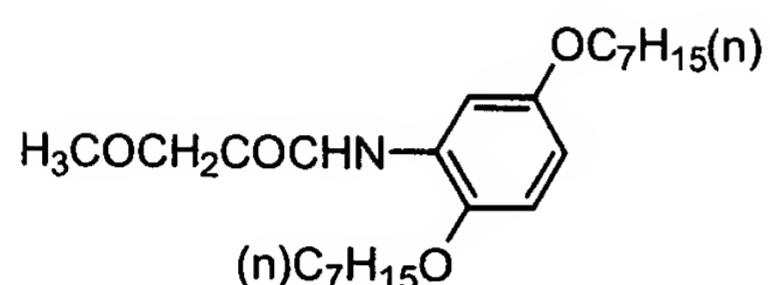
Separately, 206.3 parts of the above-mentioned alkali-treated gelatin aqueous solution were mixed with 107.3 parts of ion-exchanged water to obtain a mixture (IV).

Mixture (III) was added to mixture (IV), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion of the coupler compound was heated under reduced pressure to eliminate ethyl acetate, and was then subjected to an adjustment of concentration so as to obtain a solid content of 26.5%. The result of measurement with a particle size distribution measuring apparatus (trade name LA-700, manufactured by Horiba Co.) indicated that the obtained emulsion of the coupler compound had a median diameter of 0.21 μm .

Then, 9 parts of SBR latex (trade name: SN-307 (48% liquid), manufactured by Sumika ABS Latex Co.), adjusted to a concentration of 26.5%, were added to 100 parts of the aforementioned emulsion of coupler compound and were uniformly stirred to obtain a coupler compound emulsion (a).

[0117]

Coupler compound (C)



[0118]

<Preparation of coating solution (a)>

The microcapsule solution (a) containing the diazonium salt compound and the emulsion (a) of the coupler compound were mixed in such a manner that the mass ratio of the included coupler compound/diazonium compound became 2.2/1, thereby obtaining a coating solution (a) for the thermal recording layer.

[0119]

(2) Preparation of solution (b) for magenta
thermal recording layer

<Preparation of microcapsule solution (b) including
diazonium salt compound>

2.8 parts of a following diazonium compound (D)
(maximum absorption wavelength 365 nm); 2.8 parts of
diphenyl phthalate; 3.9 parts of phenyl 2-

benzoyloxybenzoate; 5.2 parts of a following ester compound (trade name: Light Ester TMP, manufactured by Kyoei Yushi Kagaku Co.); and 0.1 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C, 70% methanol solution, manufactured by Takemoto Oil & Fat Co., Ltd) were added to 15.1 parts of ethyl acetate and uniformly dissolved under heating. To the thus-obtained mixture, 2.5 parts of a mixture of xylylene diisocyanate/trimethylolpropane adduct and xylylene diisocyanate/bisphenol-A adduct (trade name: Takenate D119N (50% ethyl acetate solution), manufactured by Mitsui Takeda Chemicals, Inc.) and 6.8 parts of a xylylene diisocyanate/trimethylolpropane adduct (trade name: Takenate D110N (75% ethyl acetate solution) manufactured by Mitsui Takeda Chemicals, Inc.) were added as capsule wall materials and uniformly stirred to obtain a mixture (V).

[0120]

Separately, 55.3 parts of the above-mentioned phthalated gelatin aqueous solution were added to 21.0 parts of ion-exchanged water to obtain a mixture (VI).

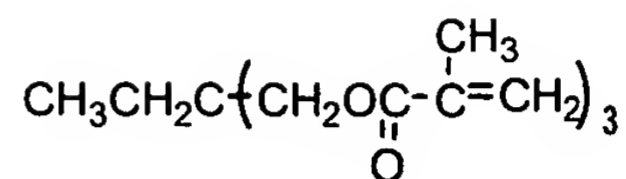
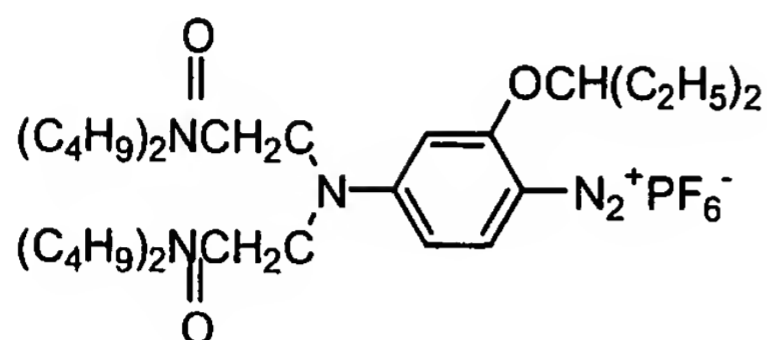
Mixture (V) was added to mixture (VI), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion was mixed

uniformly with 24 parts of water, and then subjected to an encapsulation reaction for 3 hours while stirring at 40°C and under in order to eliminate ethyl acetate. Next, 4.1 parts of an ion exchange resin (trade name: Amberlite IRA68, manufactured by Organo Corp.) and 8.2 parts of an ion exchange resin (trade name: Amberlite IRC50, manufactured by Organo Corp.) were added and the mixture was further stirred for 1 hour. Thereafter, the ion exchange resin was eliminated by filtration, and the capsule solution was subjected to an adjustment of concentration so as to obtain a solid content of 20.0%, thereby obtaining a microcapsule solution (b) containing the diazonium salt compound. The result of measurement with a particle size distribution measuring apparatus (trade name: LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of 0.43 μm .

[0121]

Diazonium compound (D)

Ester compound



[0122]

<Preparation of coupler compound emulsion (b)>

10.0 parts of a following coupler compound (E); 14.0 parts of triphenylguanidine (manufactured by Hodogaya Chemical Co., Ltd.); 14.0 parts of 4,4'-(m-phenylenediisopropylidene)-diphenol (trade name: Bisphenol M, manufactured by Mitsui Petrochemicals Inc.); 14 parts of 1,1-(p-hydroxyphenyl)-2-ethylhexane; 3.5 parts of 3,3,3',3'-tetramethyl-5,5',6,6'-tetra(1-propyloxy)-1,1'-spirobisindane; 3.5 parts of a following compound (G); 1.7 parts of tricresyl phosphate; 0.8 parts of diethyl maleate; and 4.5 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C (70% methanol solution) manufactured by Takemoto Oil & Fat Co., Ltd.) were dissolved in 36.9 parts of ethyl acetate to obtain a mixture (VII).

[0123]

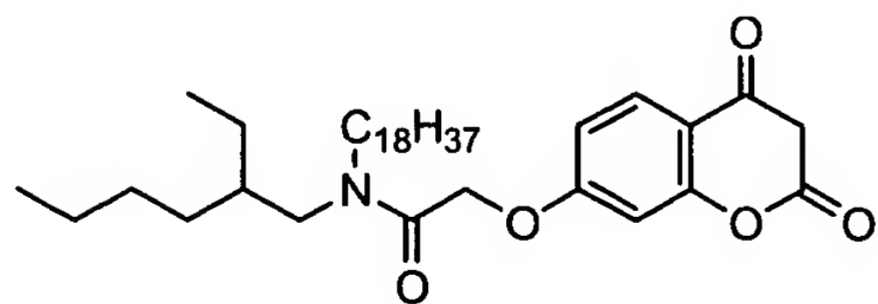
Separately, 206.3 parts of the alkali-treated

gelatin aqueous solution were mixed with 107.3 parts of ion-exchanged water to obtain a mixture (VIII).

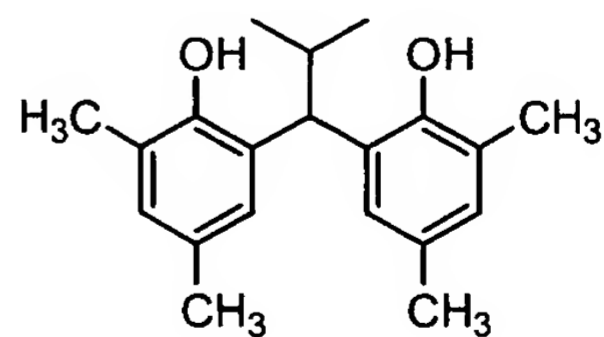
Mixture (VII) was added to mixture (VIII), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion of the coupler compound was heated under reduced pressure to eliminate ethyl acetate, and was subjected to an adjustment of concentration so as to obtain a solid content of 24.5%, thereby obtaining a coupler compound emulsion (b). The result of measurement with a particle size distribution measuring apparatus (trade name LA-700, manufactured by Horiba Co.) indicated that the obtained emulsion of the coupler compound had a median diameter of 0.22 μm .

[0124]

Coupler compound (E)



Compound (G)



[0125]

<Preparation of coating solution (b)>

The microcapsule solution (b) containing the diazonium salt compound and the emulsion (b) of the coupler compound were mixed in such a manner that the mass ratio of the included coupler compound/diazonium compound became 3.5/1. Further, an aqueous solution (5%) of polystyrenesulfonic acid (partially neutralized with potassium hydroxide) was mixed in an amount of 0.2 parts with respect to 10 parts of the capsule solution, thereby obtaining a coating solution (b) for the thermal recording layer.

[0126]

(3) Preparation of solution for cyan thermal recording layer

<Preparation of an electron donating dye precursor containing microcapsule solution (c)>

In 18.1 parts of ethyl acetate, 7.6 parts of the following electron donating dye (H); 8.0 parts of a mixture of 1-methylpropylphenyl-phenylmethane and 1-(1-methylpropyl-phenyl)-2-phenylethane (trade name: Hysol SAS-310, manufactured by Japan Oil Co., Ltd.) and 8.0 parts of a following compound (I) (trade name: Irgaperm 2140, manufactured by Ciba-Geigy Inc.) were added as capsule wall materials and uniformly dissolved under heating. To the thus-obtained mixture, 7.2 parts of a

xylylene diisocyanate/trimethylolpropane adduct (trade name: Takenate D110N (75% ethyl acetate solution) manufactured by Mitsui Takeda Chemicals, Inc.) and 5.3 parts of polymethylene polyphenyl polyisocyanate (trade name: Millionate MR-200, manufactured by Nippon Polyurethane Industries, Co., Ltd.) were added as capsule wall materials and uniformly stirred to obtain a mixture (IX).

[0127]

Separately, 9.5 parts of ion-exchanged water; 0.17 parts of 50% Scrapp AG-8, manufactured by Nippon Seika Co.); and 4.3 parts of sodium dodecylbenzenesulfonate (10% aqueous solution) were added to 28.8 parts of the above-mentioned phthalated gelatin aqueous solution to obtain a mixture (X).

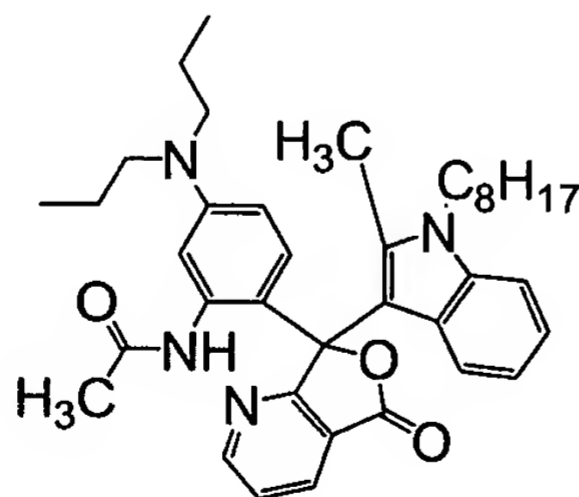
Mixture (IX) was added to mixture (X), and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 40°C. The obtained emulsion was mixed uniformly with 50 parts of water and 0.12 parts of tetraethylene pentamine, and was subjected to an encapsulation reaction for 3 hours while stirring at 65°C and eliminating ethyl acetate, and the concentration was adjusted to obtain a solid concentration of 33% in the liquid, thereby obtaining a microcapsule solution. The

result of measurement with a particle size distribution measuring apparatus (trade name LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of 1.00 μm .

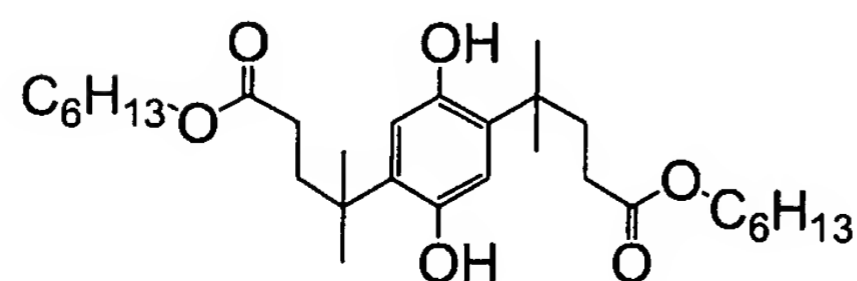
Then 100 parts of the microcapsule solution were added to 2.5 parts of a 25% aqueous solution of sodium dodecylbenzenesulfonate (trade name: NEOPELEX F-25, manufactured by Kao Corp.), and 4.2 parts of a fluorescent whitening agent containing a 4,4'-bistriazinyl-aminostylbene-2,2'-disulfon derivative (trade name: Kaycoll BXNL, manufactured by Nippon Soda Co., Ltd.) and uniformly stirred to obtain a electron donating colorless dye precursor containing microcapsule solution (c).

[0128]

Electron donating dye processor (H)



Compound (I)



[0129]

<Preparation of electron accepting compound dispersion(c)>

30.1 parts of ion-exchanged water; 15 parts of 4,4'-(p-phenylenediisopropylidene)diphenol (trade name: bisphenol P, manufactured by Mitsui Petrochemical Co.); and 3.8 parts of a 2% aqueous solution of sodium 2-ethylhexylsuccinate were added to 11.3 parts of the phthalated gelatin aqueous solution and dispersed overnight with a ball mill to obtain a dispersion. The dispersion had a solid content of 26.6 %. 100 parts of the dispersion were added with 45.2 parts of the alkali-treated gelatin aqueous solution, then stirred for 30 minutes, and were next added with ion-exchanged water so as to give a solid content of the dispersion of 23.5% thereby obtaining an electron accepting compound dispersion (c).

[0130]

<Preparation of coating solution (c)>

The electron donating dye precursor containing microcapsule solution (c) and electron accepting compound dispersion (c) were mixed such that the mass ratio of the electron accepting compound/electron donating dye precursor became 10/1, thereby obtaining a coating

solution (c).

[0131]

(4) Preparation of coating solution for intermediate layer

100.0 parts of alkali-treated low ion content gelatin (trade name: #750 gelatin, manufactured by Nitta Gelatin Inc.); 2.857 parts of 1,2-benzothiazolin-3-one (3.5% methanol solution, manufactured by Daito Chemical Industries, Ltd.); 0.25 parts of calcium hydroxide and 521.643 parts of ion-exchanged water were mixed and dissolved at 50°C to obtain an aqueous gelatin solution for preparing an intermediate layer.

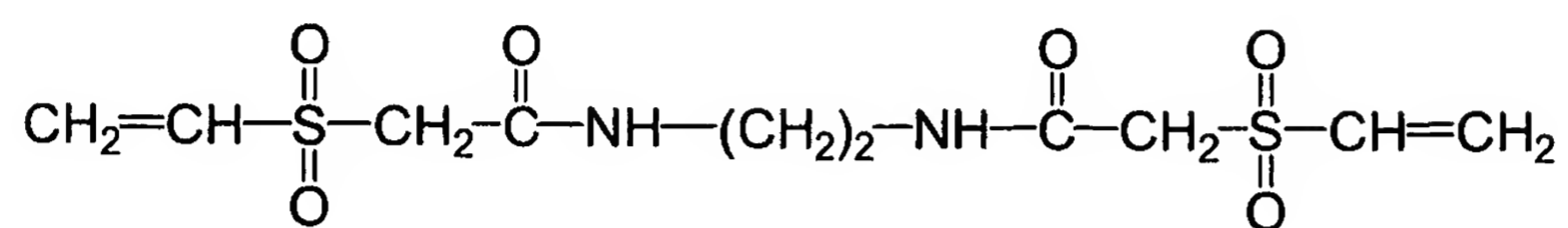
[0132]

10.0 parts of the gelatin aqueous solution for preparing the intermediate layer; 0.05 parts of sodium (4-nonylphenoxytrioxyethylene)butylsulfonate (2.0% aqueous solution, manufactured by Sankyo Chemicals Co., Ltd); 2.07 parts of boric acid (4.0% aqueous solution); 0.19 parts of an aqueous solution (5%) of polystyrenesulfonic acid (partially neutralized with potassium hydroxide); 3.42 parts of a 4% aqueous solution of the following compound (J) (manufactured by Wako Pure Chemical Ltd.); 1.13 parts of a 4% aqueous solution of the following compound (J')

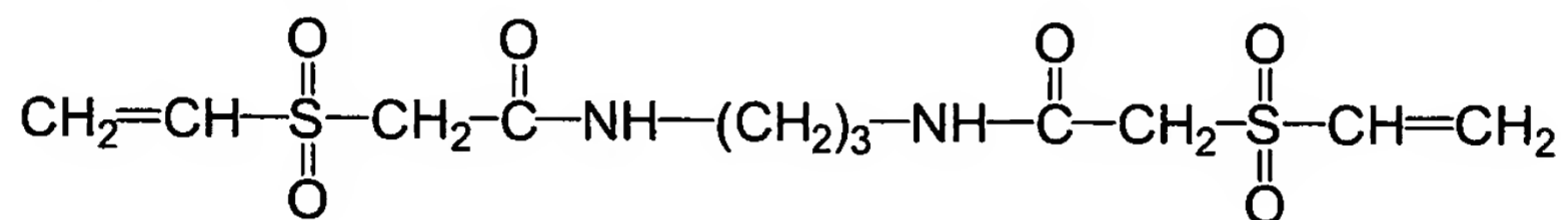
(manufactured by Wako Pure Chemical Ltd.); and 0.67 parts of ion-exchanged water were mixed to obtain a coating solution for the intermediate layer.

[0133]

Compound (J)



Compound (J')



[0134]

(5) Preparation of coating solution for optical transmittance control

<Preparation of microcapsule solution of ultraviolet absorber precursor>

14.5 parts of [2-allyl-6-(2H-benzotriazol-2-yl)-4-t-octylphenyl]benzenesulfonate as an ultraviolet absorber precursor; 2.5 parts of 2,2'-t-octylhydroquinone; 1.0 part of tricresyl phosphate; 5.7 parts of α -methylstyrene dimer (trade name: MSD-100, manufactured by Mitsui Chemicals Inc.); and 0.45 parts of calcium dodecylbenzenesulfonate (trade name: Pionin A-41-C, (70% methanol solution))

manufactured by Takemoto Oil & Fat Co., Ltd.) were uniformly dissolved in 71 parts of ethyl acetate. To this mixture were added 54.7 parts of a xylylene diisocyanate/trimethylolpropane adduct (trade name: Takenate D110N (75% ethyl acetate solution), manufactured by Mitsui Takeda Chemicals, Inc.) as a capsule wall material, and the mixture was uniformly stirred to obtain a mixture of the ultraviolet absorber precursor.

[0135]

Separately, 52 parts of itaconic acid-modified polyvinyl alcohol (trade name: KL-318, manufactured by Kuraray Co., Ltd.) were mixed with 8.9 parts of a 30% aqueous solution of phosphoric acid; and 532.6 parts of ion-exchanged water to obtain a polyvinyl alcohol (PVA) aqueous solution for a microcapsule solution of the ultraviolet absorber precursor.

[0136]

The aforementioned mixture of the ultraviolet absorber precursor was added to 516.06 parts of the aqueous PVA solution for the ultraviolet absorber precursor microcapsule solution, and was emulsified with a homogenizer (manufactured by NIPPON SEIKI Co., Ltd.) at 20°C. The obtained emulsion was added and mixed uniformly

with 254.1 parts of ion-exchanged water, and was subjected to an encapsulation reaction for 3 hours while stirring at 40°C. Thereafter, 94.3 parts of an ion exchange resin (trade name: Amberlite MB-3, manufactured by Organo Corp.) were added and the mixture was further stirred for 1 hour. Thereafter, the ion exchange resin was eliminated by filtration, and the capsule solution was subjected to an adjustment of concentration so as to obtain a solid content of 13.5%. The result of measurement with a particle size distribution measuring apparatus (trade name: LA-700, manufactured by Horiba Co.) indicated that the obtained microcapsules had a median diameter of $0.23 \pm 0.05 \mu\text{m}$. 859.1 parts of the microcapsule solution were mixed with 2.416 parts of carboxy-modified styrene-butadiene latex (trade name: SN-307 (48% aqueous solution), manufactured by Sumitomo Nogtakku) and 39.5 parts of ion-exchanged water to obtain a microcapsule solution of the ultraviolet absorber precursor.

[0137]

<Preparation of coating solution for optical transmittance control layer>

1000 parts of the microcapsule solution of the ultraviolet absorber precursor; 7.75 parts of a 4% aqueous solution of sodium hydroxide; and 73.39 parts of sodium

(4-nonylphenoxytrioxyethylene)butylsulfonate (2.0% aqueous solution, manufactured by Sankyo Chemicals Co., Ltd.) were mixed to obtain a coating solution for the light transmittance control layer.

[0138]

(6) Preparation of coating solution for protective layer

<Preparation of polyvinyl alcohol solution for protective layer>

150 parts of a vinyl alcohol-alkylvinyl ether copolymer (trade name: EP-130, manufactured by Denka Corp.); 7.5 parts of a mixture of sodium alkylsulfonate and a polyoxyethylene alkyl ether phosphoric acid ester (trade name: Neoscore CM-57 (54% aqueous solution), manufactured by Toho Chemical Industries, Co., Ltd.); 7.05 parts of an ethylene oxide adduct of acetylenediol (trade name: Dinol 604, manufactured by Air Products Japan, Inc.); 7.05 parts of a silicone surfactant (trade name: SYLGARD 309, manufactured by Toray-Dow Corning Silicone Ltd.); and 3592 parts of ion-exchanged water were mixed and uniformly dissolved for 1 hour at 90°C to obtain a polyvinyl alcohol solution for the protective layer.

[0139]

<Preparation of pigment dispersion for protective layer>

8 parts of barium sulfate (trade name: BF-21F, barium sulfate content 93% or higher, manufactured by Sakai Chemical Industries, Co.) were mixed with 0.2 parts of an anionic special polycarboxylic acid polymer surfactant (trade name: Poise 532A (40% aqueous solution), manufactured by Kao Corp.) and 11.8 parts of ion-exchanged water and were dispersed in a Dyno mill to prepare a pigment dispersion for the protective layer. The result of measurement with a particle size distribution measuring apparatus (trade name: LA-910, manufactured by Horiba Co.) indicated that the dispersion had a median diameter of 0.15 μm or less.

[0140]

<Preparation of dispersion of matting agent for protective layer>

220 parts of wheat starch (trade name: Wheat starch S, manufactured by Shinshin Shokuryo Kogyo Co.) were mixed with 3.81 parts of an aqueous dispersion of 1-2-benzisothiazolin-3-one (trade name: PROXEL B.D, manufactured by I.C.I. Ltd.) and 1976.19 parts of ion-exchanged water and were dispersed uniformly to obtain a dispersion of the matting agent for the protective layer.

[0141]

<Preparation of coating blend solution for protective layer>

1000 parts of the polyvinyl alcohol solution for the protective layer were uniformly mixed with 50 parts of sodium (4-nonylphenoxytrioxyethylene)butylsulfonate (2.0% aqueous solution, manufactured by Sankyo Chemicals, Co.); 50 parts of the pigment dispersion for the protective layer; 16.65 parts of the dispersion of the matting agent for the protective layer; 48.7 parts of a zinc stearate dispersion (trade name: Himicron LIII, 21% aqueous solution, manufactured by Chukyo Yushi Co.); 15 parts of zirconium potassium carbonate (10% aqueous solution), manufactured by Newtex Co.; and 280 parts of ion-exchanged water to obtain a coating blend solution for the protective layer.

[0142]

(7) Preparation of support

<Preparation of coating solution for undercoating layer>

40 parts of enzyme-decomposed gelatin (average molecular weight: 10,000, viscosity by PAGI method: 1.5 mPa.s (15 mP), jelly strength by PAGI method: 20 g) were mixed with 60 parts of ion-exchanged water and dissolved and stirred at 40°C to obtain an aqueous gelatin solution

for the undercoat layer.

Separately, 8 parts of water-swelling synthetic mica (aspect ratio: 1000, trade name: Somashif ME100, manufactured by Cope Chemical Inc.) were mixed with 82 parts of water and subjected to wet dispersion in a visco mill to obtain a mica dispersion with an average particle size of 2.0 μm . The mica dispersion had water added thereto so as to obtain a mica concentration of 5% and was uniformly mixed to obtain the desired mica dispersion.

[0143]

To 100 parts of the aforementioned 40% aqueous gelatin solution for a undercoating layer at 40°C, 120 parts of water and 556 parts of methanol were added and sufficiently mixed by stirring, then 208 parts of the 5% mica dispersion were added and sufficiently mixed by stirring, and 9.8 parts of a 1.66% polyethylene oxide surfactant were added thereto. Then, at a liquid temperature maintained at 35° to 40°C, 7.3 parts of a gelatin hardening agent of an epoxy compound were added to obtain a coating solution (5.7%) for the undercoat layer.

[0144]

<Preparation of support with undercoat layer>

Wood pulp, composed of 50 parts of LBPS and 50 parts

of LBPK, was beaten with a disk refiner to a Canadian freeness of 300 ml, then added thereto were 0.5 parts of epoxylated behenate amide; 1.0 part of anionic polyacrylamide; 1.5 parts of aluminum sulfate; 0.1 parts of polyamidepolyamine epichlorohydrin; and 0.5 parts of cationic polyacrylamide, each in absolute dry mass ratios to the pulp, and was subjected to paper making with a long-screen paper mill to form a base paper with a basis weight of 114 g/m², of which thickness was adjusted to 100 µm by a calendaring process.

[0145]

After a corona discharge treatment of both surfaces of the base paper, polyethylene was coated with a melt extruder so as to obtain a resin thickness of 36 µm thereby forming a resin layer of a matted surface (this surface referred to as a "rear surface"). Next, on the surface opposite to the surface bearing the above-mentioned resin layer, polyethylene containing titanium dioxide of anatase type in 10% and a small amount of Prussian blue was coated with a melt extruder so as to obtain a resin thickness of 50 µm thereby forming a resin layer with a glossy surface (this surface referred to as a "front surface"). On the polyethylene resin coated rear surface, corona discharge treatment was performed, after

which aluminum oxide (trade name: Alumina Sol 100, manufactured by Nissan Chemical Industries, Ltd.)/silicon dioxide (trade name: Snowtex-O, manufactured by Nissan Chemical Industries, Ltd.) = 1/2 (mass ratio) as an antistatic agent were dispersed in water and after drying, coated with a dry mass amount of 0.2 g/m². Then, on the polyethylene resin coated front surface, after a corona discharge treatment, the above-described coating solution for the undercoat layer was coated with a coating amount of mica of 0.26 g/m² to obtain a support with an undercoat layer.

[0146]

<Coating of a coating solution for each thermal recording layer>

On the support with the undercoat layer, seven layers were simultaneously and successively coated in order from the bottom, in the following order: the thermal recording layer coating solution (c); the intermediate layer (intermediate layer A) coating solution; the thermal recording layer coating solution (b); the intermediate layer (intermediate layer B) coating solution; the thermal recording layer coating solution (a); the coating solution for the light transmittance control layer; and the coating solution for the protective layer. These were dried under

conditions of 30°C, 30%RH and then 40°C, 30%RH to obtain a multi-color thermal recording material of an example 1.

In this operation, the thermal recording layer coating solution (a) was controlled in such a manner that the diazo compound (A) included in the solution had a solid coating amount of 0.078 g/m²; the thermal recording layer coating solution (b) was coated in such a manner that the diazo compound (D) included in the solution had a solid coating amount of 0.206 g/m²; and the cyan thermal recording layer coating solution (c) was coated in such a manner that the electron donating colorless dye precursor (H) included in the solution had a solid coating amount of 0.355 g/m².

[0147]

Also, the intermediate layer B coating solution was coated so as to have a solid coating amount of 2.39 g/m²; the intermediate layer A coating solution was coated so as to have a solid coating amount of 3.34 g/m²; the coating solution for the light transmittance control layer was coated so as to have a solid coating amount of 2.35 g/m²; and the coating solution for the protective layer was coated so as to have a solid coating amount of 1.39 g/m².

[0148]

[Example 2]

A multi-color thermal recording material of example 2 was prepared in the same manner as in example 1, except that the 15 parts of zirconium potassium carbonate (10% aqueous solution), manufactured by Newtex Co., added in the coating blend solution for the protective layer, were replaced with 10 parts of a nitrate-based zirconium compound (trade name: Zircosol HA (15% aqueous solution), manufactured by Newtex Co.).

[0149]

[Example 3]

The multi-color thermal recording material of example 3 was prepared in the same manner as in example 1, except that the 15 parts of zirconium potassium carbonate (10% aqueous solution), manufactured by Newtex Co., added in the coating blend solution for the protective layer, were replaced with 8.3 parts of zirconium sulfate (18% aqueous solution), manufactured by Newtex Co.).

[0150]

[Example 4]

The multi-color thermal recording material of example 4 was prepared in the same manner as in example 1, except that the 15 parts of zirconium potassium carbonate

(10% aqueous solution), manufactured by Newtex Co.), added in the coating blend solution for the protective layer, were replaced with 14 parts of titanium lactate (trade name: Orgatix TC-310 (8.2% aqueous solution), manufactured by Matsumoto Seiyaku Kogyo Co.).

[0151]

[Comparative Example 1]

The multi-color thermal recording material of comparative example 1 was prepared in the same manner as in the example 1, except that 2.7 parts of boric acid (4.0% aqueous solution) were added to the intermediate layer coating solution and zirconium potassium carbonate manufactured by Newtex Co. was not added in the coating blend solution for the protective layer.

[0152]

[Comparative Example 2]

The multi-color thermal recording material of comparative example 2 was prepared in the same manner as in comparative example 1, except that the amount of boric acid added to the coating solution for the intermediate layer was changed from 2.7 parts to 7.2 parts.

[0153]

[Comparative Example 3]

The multi-color thermal recording material of comparative example 3 was prepared in the same manner as in example 1, except that zirconium potassium carbonate manufactured by Newtex Co. was not added in the coating blend solution for the protective layer.

[0154]

<<Evaluation>>

The multi-color thermal recording materials of the aforementioned examples and comparative examples were subjected to the following evaluations. The obtained results are shown in Table 1.

[0155]

<Evaluation of water-resistance>

A solid black image was printed on each thermal recording material with a digital printer (trade name: NC370D, manufactured by Fuji Photo Film Co., Ltd.). Water was dropped on the printed surface of the black solid image of each thermal recording material, and immediately wiped off.

After the portion where water was dropped completely dried, evaluation was made by visual observation according to the following criteria:

A: almost no trace of water in the water-dropped portion or surrounding area thereof;

B: slight trace of water in the water-dropped portion but no trace in the surrounding area;

C: traces observable in the water-dropped portion or in the surrounding area.

[0156]

<Evaluation of image quality>

An A6-sized thermal head (model: KTJ-13 SAN24-FFA, manufactured by Kyocera Corp.) was mounted on a jig printer equipped with a platen of a diameter of 12 ϕ , a hardness of 40° and a pressure of 6 kg/cm (trade name: GX-3, manufactured by Matires Co.). When the temperature in the above-described printer was lowered to room temperature, solid images with print energies of 60 to 100 mJ/mm², changed at a step of 10 mJ/mm², were printed in the thermal head main scanning direction under conditions of a line cycle of 5.29 ms, electric power of 0.32 W, and a transport speed of 16 mm/s.

[0157]

The printed sample was evaluated by visual observation according to the following:

A: no thermalhead trace in a high energy print portion

(80 - 100 mJ/mm²) and in a low energy print portion (60 - 80 mJ/mm²);

B: a thermalhead trace of a spindle shape with a width of several hundred micrometers and a length of several millimeters, slightly different in gloss from the surrounding area, was generated in a high energy print portion;

C: an area of an amorphous shape slightly different in gloss from the surrounding area was generated in a high energy print portion;

D: a thermalhead trace shaped like B or C was generated in the entire print energy range of 60 to 100 mJ/mm².

[0158]

<Measurement of glossiness>

A black solid image was printed on each thermal recording material with a digital printer (trade name: NC370D, manufactured by Fuji Photo Film Co., Ltd.). On the print surface of the black solid image of each thermal recording material, a mirror surface glossiness was measured by a digital variable angle glossiness meter (trade name: UGV-5D, manufactured by SUGA TEST INSTRUMENTS CO., LTD.) with an incident angle of 20°.

[0159]

Table 1

	Added material	amount of addition (to PVA)	water- proof- ness	image quality	glossi- ness
Example 1	zirconium carbonate	-	A	A	46
Example 2	zirconium nitrate	-	A	B	42
Example 3	zirconium sulfate	-	A	A	48
Example 4	titanium lactate	-	B	B	40
Comp.Ex.1	-	15%	C	C	42
Comp.Ex.2	-	40%	B	B	30
Comp.Ex.3	-	-	D	D	24

[0160]

The results in Table 1 indicate that examples 1 to 4, in comparison to the comparative examples, exhibit superior water-resistance, image quality and glossiness. In particular, example 1, which employs the zirconium carbonate, and example 3, which employs the zirconium sulfate, are superior not only to the comparative examples but also to the other examples in terms of image quality and glossiness.

[0161]

[Effects of the Invention]

The present invention can provide a thermal recording material which, when printing multiple times on the same surface at high speed and with high energy, provides high glossiness, thereby enabling the recording of high-quality images.

[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

[SUMMARY]

[OBJECT]

To provide a thermal recording material having high glossiness and the capability to prevent deterioration of the printing sheet, thereby improving the durability of the thermal head and stably providing high-quality images.

[MEANS FOR SOLUTION]

A thermal recording material comprising, on a support, a thermal recording layer and a protective layer containing a water-soluble resin, wherein the thermal recording material includes a water-soluble or oil-soluble compound of a transition element of the group IVb, and preferably, the protective layer includes ultrafine inorganic particles and the compound of transition element is a water-soluble zirconium compound.

[SELECTED FIGURE]

NONE